THE ATMOSPHERIC NITROGEN INDUSTRY

WITH SPECIAL CONSIDERATION OF THE PRODUCTION OF AMMONIA AND NITRIC ACID

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PART II

TECHNICAL SECTION

CHAPTER XVIII

The Cyanamide Industry[1]

It was explained in the first Part that the production of ammonia from calcium cyanamide, and of the latter from the nitrogen of the air, is the oldest method of producing NH_3 synthetically.[2]

The first stage in the synthesis of ammonia by means of cyanamide is the production of a good calcium carbide capable of nitrogenation. This subject has been latterly dealt with, more especially by R. Taussig in Ullmann's "Encyclopædia," vol. iii., pp. 177–205.[3]

Calcium carbide, commonly known as "carbide," is, when pure, a colourless, transparent, crystalline substance of specific gravity 2·22 at 18° C. It is insoluble in all known solvents. The technical product is less pure, and has a crystalline fracture, which is iridescent in the case of better qualities, but quickly weathers by attracting water, and then acquires a dull greyish-white colour. Carbide, when freshly drawn from the furnace, is grey, brownish-yellow, or black in colour. Of the many reactions of carbide, those of main practical interest are its decomposition by water to form acetylene and lime and its power of fixing atmospheric nitrogen. Calcium carbide has a strongly reducing action on most metallic oxides, forming either the pure metal or the metallic carbide. This property of carbide was utilised during the War in the steel industry. The Deutsch-Luxemburgische Bergwerks und Hütten A.G. of Bochum, placed their deoxidation process for pig iron and steel freely at the disposal of the German steel works for the period of the War, and it was thus possible to cope to some extent with the dearth of ferro-manganese. The above-mentioned company describe their process in German Patent 300,012. The deoxidation process is so carried

[1] Compare W. Moldenhauer, "Die Reaktionen des freien Stickstoffs" (Berlin, 1920.)

[2] See F. Muhlert, "Die Industrie der Ammoniak und Cyanverbindungen" (Leipzig, 1915), pp. 204 et seq.

[3] See also R. Meingast, *Chem. Ztg.*, 1920, pp. 873 et seq.

out that the addition of calcium carbide takes place in the presence of a minimum quantity of manganese, not less than 0·2 per cent. Under these conditions calcium carbide is a perfect substitute for ferro-manganese in the Thomas and Siemens-Martin processes. The amount of carbide necessary is about 0·5 per cent. According to German pat. 298,847 the Röchlingsche Eisen und Stahlwerke G.m.b.H. and W. Rodenhauser of Völklingen-on-Saar, melt the carbide previously in a special furnace and then add it to the melt which is to be deoxidised whilst in a molten condition. (See also German pat. 300,012.) According to German pat. 300,764, S. Zuckschwerdt uses calcium cyanamide instead of carbide for the deoxidation of iron.

German pat. 138,368 of the Chem. Fabr. Griesheim-Elektron of Frankfort-a.-M., describes the decomposition of carbide with alkali fluoride at high temperatures, with production of the pure alkali metal :—

$$CaC_2 + 2\,KF = CaF_2 + K_2C_2,$$
$$K_2C_2 = 2\,K + 2\,C.$$

Metallic potassium is manufactured in this way.

German pats. 112,416 and 174,846 of A. Frank are of interest: they describe the decomposition of acetylene or calcium carbide by CO, CO_2, halogens, H_2S, and other compounds (U.S. pat. 682,472). At temperatures from 200°–250° C. graphitic carbon is formed in this way from acetylene :—

$$C_2H_2 + CO = H_2O + 3\,C.^1$$

In German pat. 96,427 F. J. Bergmann claims the decomposition of acetylene or carbide by hydrogen peroxide :—

$$C_2H_2 + H_2O_2 = C_2 + 2\,H_2O.$$

Caro has thrown doubt on the possibility of this reaction.[2]

Rossel[3] produces magnesium nitride by heating carbide with magnesium in the air; the mass becomes incandescent :—

$$CaC_2 + 3Mg + 2N + 5O = CaO + Mg_3N_2 + 2CO_2.$$

Iron, zinc and copper behave similarly to magnesium. Jacobson reduces nitrate to nitrite by means of carbide (German pat. 86,524).

Davy[4] was presumably the first to prepare carbide. Moissan described the production of carbide in the electric furnace at a

[1] See German pat. 92,801; British pat. 23,957/1847; German pat. 132,836; Caro, Ludwig u. Vogel, "Handbuch fur Acetylen" (Brunswick, 1904), p. 18; J. H. Vogel, "Das Acetylen" (Leipzig, 1911), pp. 30, 32, 229.

[2] *Journ. f. Gasbel.*, 1898, p. 689; "Handbuch für Acetylen," p. 180.

[3] *Compt. rend.*, **121**, 941.

[4] *Liebig's Annalen*, 1836, p. 144.

meeting of the Académie des Sciences on December 12th, 1892, and published further work on the subject in 1893 and 1894. Thomas L. Willson, the director of the Willson Aluminium Company, of Spray, North Carolina, had already obtained carbide accidentally when he attempted to reduce lime with coal in the electric furnace, in order to produce metallic calcium. He recorded these observations in a letter to Lord Kelvin in Glasgow on September 16th, 1892. The first patent on this subject was Willson's U.S. pat. 492,377 of February 21st, 1893, and the second was German pat. 77,168 of February 20th, 1894, in the name of Moissan's assistant, L. M. Bullier, which was granted in July, 1894, but lapsed on June 14th, 1898. The carbide industry developed from these beginnings.[1]

All other methods have become unimportant compared with the electrothermic production. Wöhler produced carbide from a zinc-calcium alloy and charcoal,[2] Winkler by the reduction of $CaCO_3$ with magnesium [3] and Travers [4] from calcium chloride, sodium and powdered graphite. De Kay-Thompson, Gonzalez and Blake [5] repeated Moissan's process of leading acetylene into a solution of calcium in liquid ammonia, and concluded that it was the best of all purely chemical methods.

As oxygen is now obtained as a by-product [6] and still awaits suitable utilisation, we may refer to the work of Borchers,[7] who burns a mixture of calcium carbonate and charcoal in oxygen. According to Taussig,[8] technical attention has already been directed to these experiments. Borchers fills a graphite crucible with alternate layers of lime and an excess of wood charcoal, and blows in pre-heated enriched air containing 35 to 50 per cent. of oxygen through two magnesite jets. According to calculations of Mallard and Le Chatelier, the following temperatures are obtained: —

(*a*) With pure oxygen . . .	3,100° C.,
(*b*) With 50 per cent. oxygen . .	2,200° C.,
(*c*) With 35 per cent. oxygen . .	1,800° C., and
(*d*) With air	1,206° C.

When pure oxygen is used, molten carbide is readily obtained; with 50 to 60 per cent. oxygen a fair quantity of crystalline carbide is obtained, but with 35 per cent. oxygen no trace of carbide is produced. It is quite possible that these purely chemical methods of

[1] *Compt rend.*, **117**, 679; **118**, 591; **138**, 243.
[2] *Liebig's Annalen*, 1863, p. 120.
[3] *Ber.*, **23**, 120 (1890).
[4] *Proc. Chem. Soc.*, **118**, 15 (1893).
[5] *Met. Chem. Eng.*, **12**, 779 (1914).
[6] *Chem. Ztg.*, 1921, pp. 74, 94.
[7] *Zeitsch. f. Elektrochemie*, 1902, p. 349.
[8] Ullmann's "Encyclopædia."

preparation may become important some day. The calcium cyanamide works all fractionate liquid air, and thus obtain large quantities of oxygen, which is largely rejected at present. It would thus be a convenience to use oxygen in the manner above mentioned, and so firstly to save a portion of the power, and secondly to utilise coke directly, instead of raw coal, as at present, for the production of current, for coke could undoubtedly replace the wood charcoal in Borchers' experiment. In his experiments on the purely electrothermic production of aluminium, Askenasy also obtained calcium carbide as a by-product.

The processes in the electric furnace take place essentially according to the four following equations: —

$$CaO + 3C = CaC_2 + CO,$$
$$CaO + C = Ca + CO,$$
$$CaC_2 \rightleftarrows Ca + 2C, \text{ and}$$
$$CaC_2 + CO \quad CaO + 3C,$$

of which the first should predominate, as it regulates the conditions of current and of yield. The current density, and therefore the temperature of the furnace, and also the proportions in which the ingredients are mixed, must be so arranged that the first equation is favoured. The heat of formation of carbide was determined by Forcrand.[1] It amounts to − 7,250 cal. when starting from diamond, and − 6,500 cal. when starting from amorphous carbon. The endothermic technical process of carbide manufacture from lime and coal or coke corresponds to the equation: —

$$CaO + 3C = CaC_2 + CO - 105{,}350 \text{ cal.}$$

Rothmund[2] found a reversion point for this reaction at about 1,620° C., below which temperature no carbide is formed, whilst at about 1,560° C. finely powdered carbide is decomposed by carbon monoxide to form lime and carbon. (See the above-mentioned German patents 112,415 and 174,846 by A. Frank.) In the formation of carbide, each temperature corresponds to a definite partial pressure of carbon monoxide. Arndt[3] found that carbide production starts below 1,600° C. The reaction is promoted by the melting of the lime at 1,900° C., as the molten material dissolves CaC_2. The carbide is pasty at first, and only becomes quite fluid at high temperatures; in the furnace, temperatures of 3,000° to 4,000° C. are attained. In order to avoid local overheating in the furnace, the mixture of lime and coke must be fed in with regularity. The maintenance of the right current density is very important, as carbide decomposes at

[1] *Compt. rend.*, 1895, p. 682.
[2] *Zeitsch. f. anorg. Chem.*, **31**, 136.
[3] See Taussig, *loc. cit.*

too high a temperature with production of "furnace smoke," which will be referred to later. Hansen[1] found that the carbide reaction commenced at 1,275° C. Quite recently O. Ruff has published important communications on the composition of various qualities of carbide and their stability at various temperatures.[2]

Calcium carbide for lighting purposes must be as pure as possible, and more particularly must contain no phosphide, silicide or arsenide. Contamination with arsenic compounds is so uncommon that we need not discuss it. On the other hand, the lime used for the manufacture of carbide often contains phosphate, silicate, sulphate, magnesia, alumina and iron oxide. In the electric furnace the phosphate is reduced to calcium phosphide, causing the finished carbide to liberate phosphine, which is dangerous and sometimes spontaneously combustible, when treated with water. According to the standards of the German Acetylene Association, the phosphine contents of acetylene must not exceed 0·04 per cent. A limestone containing more than 0·006 per cent. of phosphorus should not be used for the manufacture of carbide. In purifying acetylene, special attention has to be devoted to the associated phosphorus and arsenic compounds.[3] Magnesia and alumina cause the carbide to be viscous when molten, and thus cause difficulties in tapping, and form troublesome slags. Magnesia also increases the amount of flue dust. Silica and silicates are less objectionable.

If Al_2O_3 and MgO are absent, 5 to 6 per cent. of SiO_2 in the limestone is permissible, and does not seriously interfere with the manufacture. During the production of carbide the SiO_2 is partially converted into elementary silicon, which volatilises, and is thus removed from the furnace; the larger proportion forms ferrosilicon with the iron contents of the limestone, and this forms a "pig" at the bottom of the furnace. Rathenau[4] proposes to add iron initially for this very purpose. Large amounts of ferrosilicon endanger the hearth of the oven and depreciate the market value of the carbide. The ferrosilicon is sold by the carbide works as a by-product. The gypsum in the limestone is converted into sulphide during the process, and may give rise to the presence of hydrogen sulphide in the acetylene.

The impurities in carbide are of great importance in the calcium cyanamide industry, more particularly if the cyanamide is to be converted into ammonia and this is to be oxidised to nitric acid. In the catalytic oxidation process traces of volatile phosphorus and

[1] See Taussig, *loc. cit.*
[2] *Chem. Ztg.*, 1918, p 200; 1919, p 160.
[3] See J. H. Vogel, "Das Acetylen," pp 53 *et seq.*
[4] See Taussig, Ullmann's "Encyclopædia."

silicon compounds act as very serious contact poisons. The alkaline liquid in the autoclave decomposes the greater part of the silicon hydrides during the decomposition of the calcium cyanamide, so that the phosphorus derivatives remain as the most characteristic and dangerous impurities. J. H. Vogel [1] and N. Caro [2] repeatedly mention that, apart from inorganic compounds, complex organic sulphur compounds are sometimes produced, some of which contain both phosphorus and nitrogen ; also organic phosphorus compounds, condensation products of hydrogen sulphide, hydrogen phosphide and acetylene, and also of silicon hydrides and acetylene, all occur as impurities in acetylene. In the manufacture of ammonia from calcium cyanamide such compounds also play an important part, but their composition is at present almost entirely unknown.

Foreign substances may be introduced into the calcium carbide not only from the lime, but also from the coke. Phosphorus and sulphur are the most important impurities, and the carbide departments of the large cyanamide works have established a practice of procuring their coke from definite collieries and districts which are known to furnish supplies of suitable quality for the purpose. Wood charcoal is seldom used in carbide furnaces, but anthracite is used more frequently.

Both raw materials, quicklime and coke, are passed through rock-breakers before charging into the furnace ; the coke is dried in drums before it is crushed. The quicklime is used in pieces up to the size of a fist, and the coke of hazel-nut size. The charge is usually in the proportion of 90 parts by weight of quicklime to 65 parts of coke, mechanically mixed, automatically weighed, and then conveyed to the furnace by a belt conveyor or other suitable contrivance. The introduction of finely ground material into the furnace has been found to be entirely unsatisfactory.[3]

The quality of carbide is judged by the quantity of acetylene which is liberated by water from 1 kg. Exact details of the determination are given by E. von Drathen in *Chem. Ztg.*, 1921, p. 447. The acetylene lighting industry demands a high-quality carbide yielding at least 300 to 310 litres of crude acetylene per kilogram at 15° C. and 760 mm. pressure, whilst pure carbide would yield 348 litres. The capacity of carbide for absorbing nitrogen varies greatly. It is dependent on the degree of purity, on the temperature at which it is manufactured and drawn from the furnace, on the construction of the nitrogenation furnaces, on the duration and temperature at

[1] "Handbuch für Acetylen."
[2] *Loc. cit.*
[3] Kerger-Carlson, *Zeitsch. f. Elektrochemie*, **6**, 324.

which nitrogenation takes place, the purity of the nitrogen, the age of the carbide, and the fineness to which it is ground. With coke and lime from constant sources, uniform working conditions in the carbide and nitrogenation furnaces (that is, with the same type of furnace, same current density, same nitrogenation conditions and so forth), a carbide can be produced which shows a maximum yield of cyanamide of high percentage, per litre of acetylene evolved. It is not possible to give a definite standard for this relationship. Chemically pure carbide behaves less favourably on nitrogenation than a carbide which is not quite so pure, apparently for the reason that in the former case the fixation of nitrogen takes place so energetically that the quantities of heat which are suddenly liberated melt a large proportion of the carbide, and thus cement the whole mass so tightly together that penetration and further absorption of nitrogen is very unfavourably affected. A carbide of lesser purity, which is diluted, so to say, by free lime, excess of carbon and so forth, reacts more slowly with nitrogen, and the heat is better distributed. Thus carbide yielding about 275 to 280 litres of acetylene per kilogram usually reacts more favourably than carbide yielding 310 to 348 litres per kilogram, but, as already mentioned, a definite relationship cannot be given. The properties of the carbides have not been completely investigated. It has recently been shown, in the case of magnesium carbide,[1] that by suitable further treatment, such as heating for a considerable period, certain changes can be effected which are manifested in the character of the hydrocarbon liberated by water or acid. It may be that similar changes in composition take place in the case of calcium carbide if it is heated for some time to various temperatures or otherwise suitably treated, particularly in presence of excess of lime or of free carbon, and such changes may influence the nitrogenation process and then manifest themselves in the character of the impurities in the ammonia which is afterwards liberated from the calcium cyanamide. If it is true that heavy metals, in particular, hinder nitrogenation, then the electromagnetic treatment of ground carbide before nitrogenation might have a favourable influence, as it would remove the larger part of the iron-bearing compounds, such as ferrosilicon, carbo-ferrosilicon, and so forth.

In the block process carbide furnaces are used in which a large block of molten carbide is produced. The process is then dis-

[1] See lecture by Fr. Fischer, "Die Kohle als Quelle neuer Chemischer Rohstoffe," General meeting of Verein deutsch Chemiker, September 9th, 1920, Hanover; *Brennstoff Chemie*, 1920, p 51.

continued and the block removed from the furnace, which is then recharged. On the other hand, the modern tapping process works quite continuously; fresh raw materials are continually added above, whilst the liquid carbide is drawn off from time to time below (see German Patent 326,229).

Furnaces constructed to work the first type of process are those

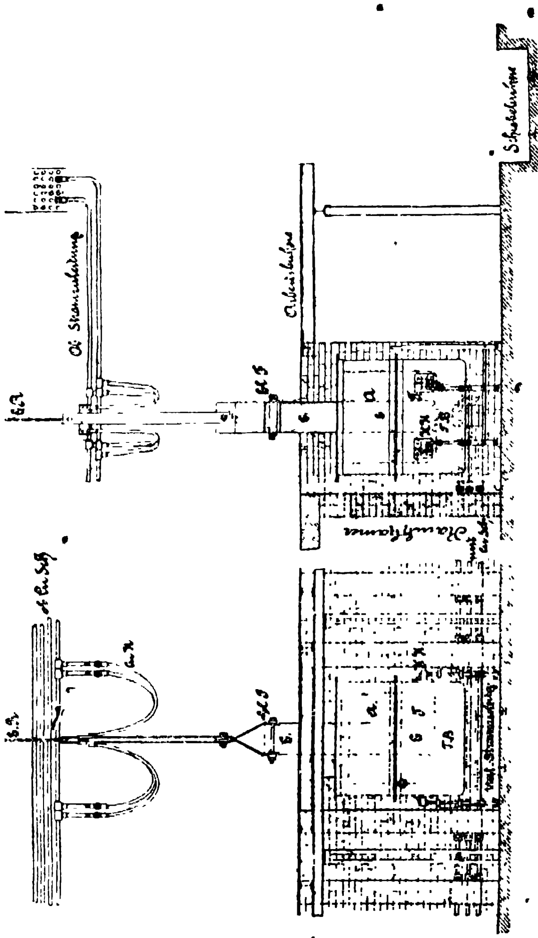


FIG. 3.

Obere Stromzuleitung = Upper bus bars. Arbeitsbuhne = Service platform.
Untere Stromzuleitung = Lower electrode. Schiebebuhne = Rail-track.
Rauch Kammer = Flue

of Bullier, Gin and Leleux, at Meran; Schuckert, at Jajce, Lonza and Hafslund; also those of Siemens and Halske at Lechbruck and other places. The works at Vallorbe had originally Bullier furnaces; the Nürnberg block furnace of Schuckert was used in Gampel, Jajce and Hafslund until 1906. In principle these types of furnace were all similar. They usually consisted of transportable box-like iron crucibles,

the floors of which were covered with plates of carbon or with carbon bricks, whilst the seams and the conducting connection between the casing and the actual crucible were formed of a mixture of powdered graphite or coal with tar. In order to carbonise the tar and unite the whole mass, and so obtain perfect conduction of the current, the crucibles were burnt in a special furnace. The crucible, which was placed on a low trolley, which served as a conductor of the current, was passed into a brickwork shaft about 2 m. high, provided with openings for the introduction of raw materials and for the removal of the furnace gases. The other electrode, supported by a pulley block, was lowered into the furnace from above. The various types of furnace differed essentially only in the character of the transmission of the current from below. Usually several furnaces were arranged in series. In Jajce three furnaces were supplied by one 1,000 h.p. three-phase generator, with one phase for each furnace. Fig. 3 depicts a Nürnberg block furnace of the older type, as used in Jajce. The electrode, *E*, receives current from the upper bus-bar, *ob, CuSch.*, through a cable, *CuK*. The electrode, *E*, is fastened to *Fl.F*, and can be raised or lowered by *E.R.* It is suspended in the interior, *A*, of the crucible, *T*, the floor, *TB*, of which forms the other electrode, which is connected to the lower bus-bar, *unt. CuSch.* through the cable *KK*. The carbide works erected at Jajce in 1898 initially contained six batteries of furnaces, each containing six units (see Fig. 4). Later 8,000 h.p. were employed, 24 furnaces being in operation and 12 in reserve. In 1906 the 36 furnaces were replaced by modern furnaces of

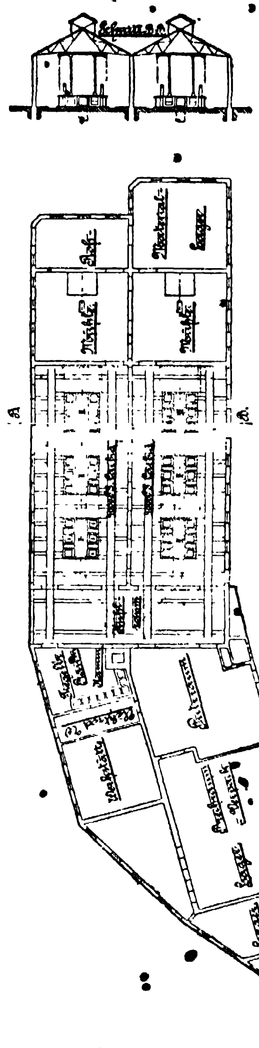


Fig. 4.

Werkstatte = Workshop. Brechraum u. Verpack = Crushers and stores.
Tiegelb. Raum = Crucible shop. Kuhlraum = Cooling chamber.
Lager = Store. Muhle = Grinding mill.
Roh-Material Lager = Stores for raw materials.

8,000 h.p., which took up only one-sixth of the area of the old furnaces.

The furnaces which were first used for the block process worked at 100 to 300 h.p., and in 1897 furnaces of 300 to 400 h.p. were considered to be very large. The disadvantages associated with block furnaces were high wages, frequent repairs, poor thermal efficiency, small yield, due to furnace smoke, and poor power efficiency, the output being at most 3·5 to 4·2 kg. of carbide per kilowatt day. As, however, a beautifully crystalline product was obtained in block furnaces, which also underwent a kind of purification by segregation in the furnace, the furnaces were predominantly used for many years.

The introduction of series furnaces represented a considerable advance; in these the lower electrode was omitted and the current was introduced through two electrodes suspended in the crucible. The Horry furnace described by Haber,[1] of the Union Carbide Company (German Patent 98,974), is a series furnace.

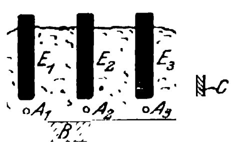


Fig.

The induction furnace recommended by Erlwein and Engelhardt (German Patent 206,175), which contains no electrodes, did not establish itself in practice, as it did not permit of the utilisation of large aggregates.

The credit of first successfully developing continuous working is due to Helfenstein, who developed his tapping process with electrical melting at Jajce. A Helfenstein furnace of 8,000 h.p. was erected at Jajce in 1906. The large open furnace of high capacity is only constructed as a three-phase furnace. It consists essentially (Fig. 5) of a shaft, the sides of which are lined with chamotte, whilst the floor is lined with kieselguhr. A graphitised mass of carbon, *B*, is firmly stamped into the floor of the furnace and forms one electrode. Three adjustable electrode bundles, *E*1, *E*2, *E*3, are suspended in the furnace; their height can be regulated, and they are supplied with three-phase current. This arrangement was covered by a French patent by Bertholus, of Bellegarde, France. The furnace is usually covered externally with an iron casing with the necessary reinforcements. Shallow three-phase furnaces on the Tophani system, taking a maximum load of 3,000 h.p., are used in France, Italy and Canada.

The Helfenstein furnace already described may be considered as typical, although details, such as the positions of the transformers, may vary. The highest load per electrode bundle is 3,000 k.w.,

[1] *Zeitsch. f. Elektrochemie*, **9**, 358.

but it is possible to increase the capacity of the furnace indefinitely by placing a number of three-phase units in series in one shaft. Thus at Hafslund 24,000-h.p. furnaces are used, containing two three-phase units in each furnace. A higher load than 3,000 k.w. per electrode bundle is not possible, as the heat evolution then becomes too high, and the smoke production becomes too inconvenient.

H. Goldschmidt [1] gives the following figures for a modern Helfenstein furnace used in Switzerland: This is open at the top, about 9 m. long, 2·5 m. deep, and 3·5 m. broad. The three electrodes are 1·8 m. long, 1·5 m. wide, and 0·5 m. thick; the width of the central electrode is 2 m. The three electrodes are in one plane, and take 40,000 amps. When 50,000 to 60,000 amps. are supplied, it is almost impossible to remain on the platform of the furnace. The E.M.F. is 120 to 160 volts. The electrodes are raised and lowered by an electro-mechanical arrangement which may be regulated automatically in such a manner that a definite interval is maintained between the sole of the furnace and the bottom of the electrodes, in spite of the wastage of the latter. This distance is on the average 20 to 50 cm.

The charging of the furnaces is far from satisfactory. It is almost exclusively carried out by hand by workmen who shovel the mixed charge into the furnace from the platform. Flames of carbon monoxide have to be quenched at once by covering with the charge. The platform is well ventilated. A satisfactory charging machine has not yet been invented.

The electrode bundles are formed from three to four parts, which are fastened together by pegs and a cement of graphite and water-glass. A normal bundle may consist, for example, of three individual electrodes, the dimensions of each being 500 × 500 × 1,000 mm. At a load of 8 to 10 amps. per square centimetre the electrodes become red-hot, and such a load should, therefore, never be exceeded. An average temperature of 2,400° to 3,000° C. for the production of carbide in the furnace corresponds to a current density in the electrode of 1 to 2 amps. per square centimetre. Such a low current density is, however, only possible at 30 to 35 volts, whilst to-day 90 volts is considered a minimum. In order to maintain a definite temperature in the furnace, the current density must be increased with rising voltage and diminished with falling voltage. An industrial carbide furnace acts both as an arc and a resistance furnace.

Acheson graphite is too dear to be used for electrodes, even in the United States. Ordinary carbon electrodes are therefore used, and both hard and soft varieties have their supporters. The develop-

[1] *Zeitsch. d. Ver. Deutscher. Ing.*, 1919, p. 87[illegible].

ment of a flourishing carbon electrode industry in Germany during the War is very largely due to the growth of the carbide industry;[1] carbon electrodes are now manufactured at the works of Gebr. Siemens & Co., at Berlin-Lichtenberg, the Planiawerke at Ratibor in Upper Silesia, the Gesellschaft für Teerverwertung m.b.H. at Duisburg-Meiderich and Rauxel, the firm of C. Conradty at Röthenbach, near Nürnberg, and Kolbermoor, near Aibling, and the Rheinische Elektrodenfabrik G.m.b.H., of Knapsack, near Cologne.[2] (See also German Patent 322,043.) In a three-phase furnace the three electrode bundles are unevenly attacked. The mean life of those carrying the first and second phases is about 50 hours, and that of the third or dead phase about 70 hours. The amount of electrode wastage varies. In the *Journal of the Society of Chemical Industry* of August, 1919, Allmand and Williams give a figure of 50 kg. of electrode wastage per ton of carbide; at the American plant at Muscle Shoals, 35 kg. are allowed per metric ton,[3] and E. R. Besemfelder[4] estimates the wastage of electrodes in the Frank-Caro process under German conditions at about 55 kg. per ton. The block furnace consumed 90 kg. of electrode carbon per ton of carbide. It is naturally difficult to give a definite figure, as this varies with numerous factors, such as the height of the charge, the quality of the material, care exercised by the workpeople, and so on; for example, the more uniform the quality of the electrode bundle the less is the loss. The Gesellschaft fur Teerverwertung, of Duisburg-Meiderich, therefore proposes in German Patent 294,135 to unite the individual electrodes to a bundle before burning, and subsequently to graphitise them.

A tap hole is situated below each of the three electrodes (see Fig. 5, A_1 to A_3), and is opened by melting the material with an auxiliary electrode. For tapping large furnaces an auxiliary carbon electrode is used of 10 to 20 cm. diameter, which receives a current of 2,000 to 4,000 amps. at 70 to 80 volts. It is carried by means of a movable stand to the tap hole, which has a diameter of about 20 cm., so that it allows of the escape of pasty material. The current for the auxiliary electrode is usually supplied from one of the phases of the furnace, and the production therefore suffers. In very large furnaces the power required by the auxiliary electrode—namely, 150 to 300 h.p.—scarcely affects the output. The auxiliary electrode softens the contents of the tap hole by arc and resistance heating, and the tap hole is then pierced by four to six powerful men using a

[1] See K. Arndt, *Chem. Ind.*, 1919, Nos. 22–23.
[2] See *Chem. Ztg.*, 1919, p. 883, and O. Dietsche, *Chem. Ztg.*, 1920, p. 36.
[3] *Chem. Met. Eng.*, 1919, p. 8.
[4] *Chem. Ztg.*, 1919, pp. 281, 522, 604, 865.

long iron rod. The carbon consumption of the auxiliary electrode is about 1 to 2 kg. per ton of carbide. The liquid carbide flows over an air-cooled, cast-iron sill, which is protected by a coating of carbide, into shallow cast-iron pans, and is then conveyed by cranes or small trucks into large cooling chambers, where it remains for twenty-four hours. Each pan holds about 500 kg. of carbide.

The electrode holders, which effect the passage of the current from the main to the head of the electrode, play a large part in carbide manufacture. In the earlier small furnaces the conduction of the current was easily effected by screwing lateral copper and iron cheeks to the head of the electrode. In large furnaces, water-cooled holders of cast iron are now used, which are fitted with cooling systems. The mounting of these holders and of the electrode bundles has to be very carefully carried out. In spite of the cooling, the contact surfaces are not loaded with more than 4 to 6 amps. per square centimetre, and the copper cables to the holders with 1 to 2 amps. per square centimetre cross-section. It is more expensive to conduct current through clamps. Jul. Baumann, of the Osterr. Verein für Chem. und Metallurg. Produktion in Schwaz, Austria, describes the various varieties of electrode holders in the *Chem. Ztg.*, 1920, pp. 33–35: in the course of this article, he points out a fact which is often overlooked, that in certain circumstances the cooling water may lead to considerable current loss by conduction. The quantities of water which are required for effective cooling are very considerable, and may amount to 100,000 cu. m. per day for a large carbide plant with an output of 300 to 350 tons daily. Jul. Baumann proposed to solve the old problem of a well-cooled electrode holder by means of a water spray.[1] In the article referred to, he considers in detail the various causes of excessive electrode consumption and the utilisation of the waste electrode heads. He also drew up an electrothermic balance for the carbide process, which should theoretically require about 360 k.w.h. per 100 kg. of an 80 per cent. product, yielding 300 to 310 litres of acetylene per kilogram; in practice 400 k.w.h. are necessary, on account of radiation losses.

H. Goldschmidt[2] states that 3·5 to 4 k.w.h. are needed per kilogram of carbide, and R. Taussig[3] assumes the following figures:—

The quantities of carbide yielding 305 litres of acetylene per kilogram at 760 mm. and 17° C. obtained per kilowatt day are:—

[1] See *Chem. Ztg.* 1920, p. 34.
[2] *Zeitsch. d. Ver. Deutsch Ing.*, 1919, p. 887.
[3] F. Ullmann's "Encyclopædia," vol. iii., p. 202.

In small block furnaces	3·5 kg. (1 kg. = 6·86 k.w.h.).
In small tapping furnaces	4·2 kg. (1 kg. carbide = 5·71 k.w.h.).
In 4,000-h.p. furnaces.	5·6 kg. (1 kg. carbide = 4·28 k.w.h.).
In 6,000-h.p. furnaces.	6·0 kg. (1 kg. carbide = 4·00 k.w.h.).

In large furnaces 1·5 tons of carbide are produced on an average per horse-power year. Carbide of lower quality can, of course, be produced with less current. R. Taussig gives an interesting diagram of Keller on this matter, to which we may refer.

In dealing with the economics of the process, data on the amounts of raw material used in small block furnaces and in tapping furnaces of over 1,000 h.p. capacity per ton of carbide produced of a definite quality are important. The quantities required are :—

Block Furnaces.		Tapping Furnaces.
800 to 1,050 kg.	Coke	600 to 700 kg.
800 ,, 1,050 ,,	Anthracite	640 ,, 700 ,,
1,200 ,, 1,500 ,,	Wood charcoal	800 ,, 950 ,,
1,080 ,, 1,200 ,,	Lime	920 ,, 1,050 ,,
40 ,, 70 ,,	Electrodes	10 ,, 40 ,,

On the basis of the prices obtaining in 1913–14, the total costs per 100 kg. of carbide in small furnaces were, therefore, 15 to 17 marks, and in tapping furnaces from 12·75 to 13·50 marks.

Covered furnaces work more cheaply, but for various reasons are still used to a relatively small extent. According to Taussig [1] the cost price per ton of carbide ready packed at the works is 132·96 marks in an open furnace, and 112·25 marks in a closed furnace, at pre-war prices. According to his calculations, the following raw materials are required per ton of carbide :—

In Open Furnace.		In Closed Furnace.
670 kg.	Anthracite	670 kg.
1,030 ,,	Lime	950 ,,
32·9 ,,	Electrodes	20 ,,
170 k.w. days	Current	150 k.w. days.

A price of 40 marks per horse-power year is assumed ; the wages bill per ton of carbide is 43·6 per cent. less for the closed furnace than with the open furnace, and auxiliary materials 74·5 per cent. less.

As the heating capacity of the current only is used in carbide manufacture, it is theoretically indifferent whether one works with direct or alternating current. Direct current offers certain advantages, as there can be no phase distortion, and therefore a lower voltage can be used for an equal number of amps. It is, however, more expensive to produce, and cannot be transformed, so that

[1] *Loc. cit.*

transmission costs are higher. Three-phase current is desirable for large furnaces, as it can be carried at high tension right up to the transformer, close to the furnace. The difficulties which are caused by phase distortion have been diminished by enlarging the generators and by other measures. According to Taussig, the efficiency, cos ϕ, in the Helfenstein furnaces attains a maximum of 0·8 at fifty periods, when each phase is at 40,000 to 50,000 amps., at a furnace voltage of 85 to 90 volts. In the case of three-phase current and large units, furnaces with three hearths represent the simplest arrangement, whilst when direct or one-phase current is used two-hearth furnaces are the most suitable. Open-hearth furnaces are

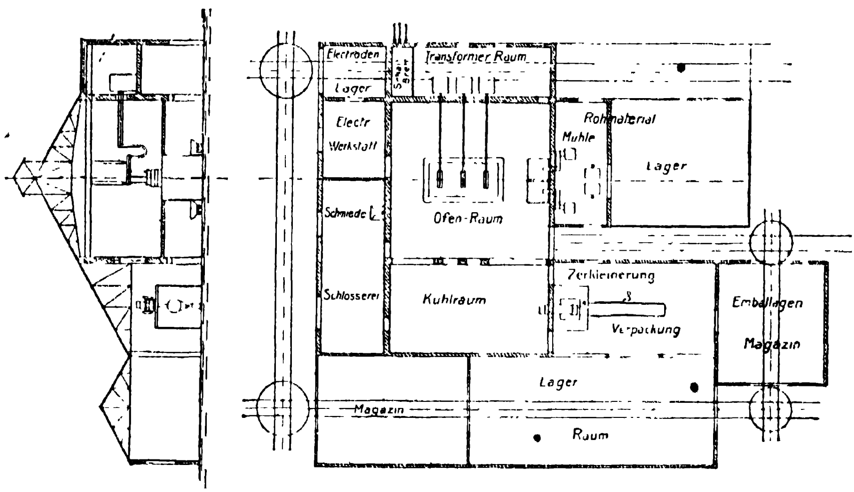


FIG. 6.

Lager—Store. Schmiede—Smithy. Muhle Mill. Werkstatt Workshop. Zerkleinerung—Crushers.

only constructed when very small amounts of current are to be used. Fig. 6 shows a modern 12,000 h.p. plant.

There is no material which stands the great heat of the electric arc indefinitely, but the very high temperature is confined to such a small space that furnace walls 1 m. distant from the electrodes are scarcely affected by the internal conditions. Large furnaces are almost always built of rectangular cross-section. In order to be able to adjust the current suitably in case of irregular working and so forth, the furnace transformers are frequently constructed in several voltage stages, so that even the smallest current density can be obtained by simple switchboard operations. The same result is also achieved by using smaller electrode bundles. Such current variations are especially important where the carbide furnaces are attached to electric power stations to equalise the power load. Short stoppages

of manufacture do not damage the furnace, but repeated long stoppages have an injurious effect, and in any case will influence the quality of the carbide which is produced, which then becomes very uneven.

In the case of three-phase furnaces, more particularly those of covered type, the electrode bundles may be changed and renewed by switching off the corresponding current phase and using the others at reduced current density.

There are only a few recent patents which deal with carbide manufacture itself, such as German patent 283,276, of the Bosnische Elektrizitäts A.G., of Vienna. There are a larger number of patents dealing with the transmission of power to the furnace, such as German patent 292,109 of the same firm, and with the electrode holders, such as German patent 313,852 of the Bayrische Stickstoff-Werke A.G. The most important problem is, however, that of a durable cover to the furnace, which is closely connected with the problem of utilising the carbon monoxide of the furnace gases and of a reliable charging contrivance. Naturally the subject cannot here be discussed in all its details, but we may refer to the fact that the future of the electric carbide furnace is closely concerned with the utilisation of the valuable carbon monoxide of the furnace gases. Covered furnaces permit of such utilisation, facilitate the handling of large quantities of material, prevent the very injurious furnace fumes, and enable the furnaces to be worked more economically and at a lower production cost than open furnaces, as is shown by the comparative figures which we have already given. Unfortunately, the technical solution of the problem is far from simple. No one has so far succeeded in constructing a large furnace cover which is sufficiently durable permanently to withstand the enormous heat radiation of the furnace. After a comparatively short life, the cover always breaks down. So far Helfenstein has been the most successful in his solution of the problem; his German Patents 224,478, 226,956, 229,302 and 235,061, describe the construction of covered furnaces and suitable charging arrangements. The electric furnace allows the current to be introduced in an equally simple manner if it is constructed in the form of several separate furnace shafts, as is shown in Fig. 7. The hearth electrode is common to all three shafts. It is then a much simpler problem to cover the individual small shafts, and the durability of the life of the covers is increased by the use of water-cooled iron supports, as described in German Patent 235,061. According to German Patent 224,878, the individual shafts are arranged at the corners of a triangle, and may then be simultaneously utilised for the manufacture of various products, for example, carbide and ferro-

silicon. R. Taussig[1] gives further details and a number of drawings. Special forms of electric furnace for the production of carbide are described by A. Petersson in German Patents 223,509 and 238,976. A. Walter (German Patent 321,127) utilises the furnace gases within the furnace itself for burning limestone.

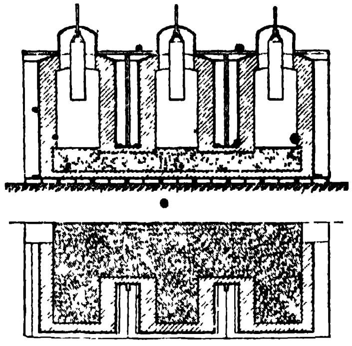


FIG. 7.

The production cost of carbide depends on a good yield and cheap electric power and wages. H. Goldschmidt[2] estimates the pre-war production costs per ton of carbide at 80 marks (£4) with cheap water power, very good yields, and low wages. According to him, the Bavarian carbide works were able to produce at this price even during the War, but presumably without allowing for amortisation and interest. When steam power is used, he estimates the production costs at about 120 marks (£6) per ton; these figures correspond well with those of Taussig, which we have already given, and which include packing. The production cost has naturally increased considerably since the introduction of the eight-hour day and also through the immense increase in cost of all raw materials.

The first association of carbide manufacturers was the Comptoir Français du Carbure, which was followed by the formation of an Italian syndicate and of the Nürnberg Syndicate, which latter included the Swiss, Austrian, German and Scandinavian manufacturers. International trade in carbide was regulated by agreement between the three groups. At the outbreak of war most of these arrangements lapsed, and the Carbide Syndicate was dissolved in 1915. We must refer to Taussig's paper[3] for further details on the production of the individual countries, on protective tariffs, and so forth. In Germany at present there exists the Vereinigten Deutschen Carbidfabriken G.m.b.H., of Berlin, and the Verband der Carbidgrosshändler Deutschlands at Böblingen, near Stuttgart. The control of carbide has practically ceased since August 1st, 1920, and the price has dropped to 350 to 370 marks per 100 kg. nett, according to the size.[4] The prices are c.i.f. at works.

Pure carbide contains 62·5 per cent. of Ca and 37·5 per cent. of

[1] Ullmann's "Encyclopædia."
[2] *Zeitsch. d. Ver. Deutsch. Ing.*, 1919, p. 887.
[3] Ullmann's "Encyclopædia."
[4] *Zeitsch. f. angew. Chem.*, 1920, ii., 298, 451; *Chem. Ztg.*, 1920, pp. 568, 583, 892; *Metallborse*, 1920, pp. 1279, 1950, 2103.

C. Commercial carbide, for the production of acetylene, contains 10 to 14 per cent. of impurities. N. Caro[1] gives the following analysis of a carbide for the manufacture of cyanamide :—

	Per cent.
CaC_2	82·30
C	1·20
CaO	14·60
CaSi	0·06
Ca_3P_2	0·07
CaS	0·13
FeSi	0·72
Undetermined	0·80

For use in the acetylene lighting industry the carbide from the cooling sheds, in which the calcium carbide contents usually diminish slightly, particularly in damp weather, is granulated, sorted, and usually packed in lead-lined iron drums. (See German Patent 300,586). If intended for cyanamide manufacture the carbide must be very finely ground. For this purpose the ordinary methods applied to hard materials are used.[2] The carbide from the cooling sheds, which has first been broken into comparatively large pieces, is usually conveyed to the crushers by a crane; it then usually passes through cast-steel rolls and then into mills, where it is extremely finely crushed. In large modern installations the carbide is transported entirely by mechanical means, such as conveyors, storage bins being provided between the various stages; these serve as a reserve and to equalise the quality. The carbide is usually ground to fine dust; this is necessary in order to ensure nitrogenation. It is, however, desirable to pass an inert gas, preferably nitrogen, through the mills, in order to minimise the danger of explosion of the mixture of carbide dust and air (German Patent 211,067). Carbon tetrachloride may be used to extinguish any fires. The firm of G. Polysius, Dessau, recommends the use of waste gases from lime kilns instead of nitrogen (German Patent 312,685). The ground material is usually transported to the place where it is to be nitrogenated by screw conveyors.

Before dealing with the nitrogenation process we will consider the problem of the removal of smoke in carbide works; these fumes form a high smoke column which is evident to the eye for a long distance from the furnaces.

Julius Baumann[3] distinguishes two components of carbide smoke. The dust, which is produced mechanically during the

[1] *Zeitsch. f. angew. Chem.*, 1909, p. 179.
[2] See C. Naske, "Zerkleinerungsvorrichtungen und Mahlanlagen," 3rd ed., (Leipzig, 1921).
[3] *Chem. Ztg.*, 1920, pp. 33-35.

crushing of the coke and lime, is blown out of the furnace by the arc before it melts. This effect increases in magnitude with the voltage of the furnace; by reducing the voltage from 75 volts (Schuckert system) to 40 volts, it is quite appreciably reduced (Baumann, 1903). The amount of this dust can be considerably reduced by suitable arrangement of the crushing and transporting devices—for example, by the use of grids, which allow lumps only to be used; it may also be removed by cyclones and similar apparatus. The second kind of furnace smoke is more dangerous. The temperatures of formation, of melting, and of decomposition of carbide, unfortunately lie very close together. Therefore, especially if too high a current density is used, it may happen that the carbide which is produced is dissociated into calcium and carbon, causing considerable loss of energy. The carbon remains in the carbide and renders this viscous and of low quality. On decomposing with water, such carbide does not give an almost white sludge, as is the case with normal qualities, but a grey or black sludge, or one discoloured by black granules. The liberated metallic calcium volatilises and burns above the furnace, with evolution of a considerable quantity of heat and production of sticky, heavy, thick and persistent fumes of calcium oxide. So far all attempts to retain these fumes even by electrostatic methods have failed. According to Baumann, the only remedy is to reduce the components of the fumes to a minimum by rational operation of the furnace. Local overheating must be avoided by controlling the current density along the electrodes. An experiment carried out by Baumann [1] with a graphite electrode showed conclusively that the temperature of the melt, and consequent depreciation of the quality of the carbide and smoke production, increases with the current passing through the electrode.

We owe to P. Schläpfer,[2] the Director of the Federal Fuel-Testing Station in Zürich, detailed information on the composition of carbide furnace smoke and of the furnace dust; very little other information on this subject has been published.

A series of analyses of the gases evolved from a three-phase furnace fed with lean coal or anthracite shows that the composition of these gases approximates more closely to that of lighting gas with increasing distance from the reaction zone. In four samples the percentage of carbon monoxide varied from 16·33 to 84·64. From Charles Bingham's book, "The Manufacture of Carbide of Calcium," Schläpfer quotes the following analysis of gases from a closed furnace :—

[1] *Loc. cit.*
[2] *Zeitsch. f. Elektrochemie*, 1919, pp. 409 *et seq.*

	Volumes per cent.
CO_2	0·0
CO	65·8
H_2	30·9
CH_4	2·0
N_2	1·3

Gases from the interior of carbide furnaces using coke contain 90 per cent. of carbon monoxide. From the reaction zone, in which 28 kg. of carbon monoxide are theoretically produced per 64 kg. of pure CaC_2, these gases rise rapidly and burn in an open furnace as soon as they come into contact with the air and at the same time are considerably diluted. At the top of the furnace carbon monoxide can hardly be detected ; one metre above the top the composition of three samples was as follows :—

	I. Volumes per cent.	II. Volumes per cent.	III. Volumes per cent.
CO_2	2·4	2·4	2·4
O_2	19·4	18·0	18·0
CO	0·0	0·0	0·0

The theoretical proportion of CO_2 is 23 to 27 per cent. The dilution is so considerable and the combustion of the poisonous constituents, such as carbon monoxide and the hydrides of arsenic, phosphorus and sulphur, is so complete, that the gases are not in themselves harmful to vegetation. The analyses show, however, that it is quite impossible to utilise the flue gases from an open furnace as a fuel, as they scarcely contain any further carbon monoxide. Their heat could at most be utilised for drying purposes or for indirect pre-heating of the gases. The circumstances are, however, quite different in the case of the closed furnace, which may therefore be considered as the furnace of the future.

Schläpfer gives three analyses of flue dust which he has obtained from three points in a carbide furnace plant, namely :—

(1) From the settling tank below the scrubber of a Körting purifier.

(2) From the large dust catcher above the first scrubber.

(3) From a coke tower used to filter the carbide furnace gases.

The analyses gave the results (in percentages) shown in the tables on p. 351.

Alkali salts, were not determined. They had been removed by solution in water from the product in the settling tank. The free calcium oxide suspended in the flue gases has been largely changed into carbonate in the settling tank and in the suction dust catcher or by the carbon dioxide of the gases. In the flue dust

A. *Soluble in Hydrochloric Acid*

	Settling Tank.	Flue Dust.	Coke Tower.
Magnesium carbonate	4·27	4·62	3·03
Calcium carbonate	72·28	39·45	12·54
Calcium oxide	7·33	15·44	24·44
Calcium sulphate	1·96	8·55	3·09
Iron oxide	5·29	4·82	4·66
Silica	4·86	4·66	3·77
	95·99	77·54	51·53

B. *Insoluble in Hydrochloric Acid*

	Settling Tank.	Flue Dust.	Coke Tower.
Ash	1·52	7·29	9·58
Carbon	2·77	2·88	34·84
Hydrogen	0·04	0·14	0·49
Sulphur and oxygen	0·19	0·17	2·11
	4·52	10·48	47·02

of the coke tower this saturation has not been carried nearly so far. The portion insoluble in acid contains the combustible constituents, which would not amount to more than 10 per cent. at most, of the original flue dust.

In the sample from the coke tower, flue dust and coke dust from the filter tower are both present. Bingham [1] gives the following analysis of carbide flue dust :—

	Per cent.
$CaCO_3$	36·4
CaO	36·3
Al_2O_3	8·0
Fe_2O_3	6·0
SiO_2	4·0
$CaSO_4$	1·6
C	7·0
MgO	Trace
H_2O	0·4
	99·7

[1] *Loc. cit.*

Should the lime contain much magnesia, most of this is converted into flue dust in so far as it does not form a slag with the silica. Bingham allows for 5 kg. of flue dust per ton of carbide produced at low voltage (see also Schläpfer). The proportion of flue dust increases considerably as the furnace voltage and the size of the furnace are increased. It is also dependent on the quality of the coke and the lime. Coarsely crushed lime causes the smallest development of flue dust.

Schläpfer [1] gives the following balance of materials for the production of 1 ton of carbide :—

(1) Materials added :—
- 1,000 kg. lime.
- 600 kg. coke.
- 28 kg. electrode carbon.

(2) Production :—
- 1,000 kg. of 85 per cent. carbide.

(3) Unutilised by-products (waste from crushing, flue dust, etc.) :
- 121 kg. lime dust.
- 60 kg. coke ash.
- 23 kg. coke dust.

(4) Substances evolved as gases : —
- 372 kg. carbon monoxide.
- 24 kg. of oxygen, hydrogen and nitrogen, also sulphur from the anthracite or coke.
- 28 kg. carbon from electrodes.

This balance of materials is, of course, only approximate ; the thermal balance sheet shows that in technical carbide manufacture considerable quantities of heat are also lost. The gases from a closed furnace produce as much heat on combustion as should suffice to burn half the limestone necessary for manufacture. (C. Aberg, of Helsingborg, calculates that 70 per cent. of the fuel could be saved.[2]) The electric furnace itself is not suitable for burning limestone ; otherwise it would be much simpler to charge it with limestone rather than quicklime.

During the last few years many experiments have been made, some of them on a considerable scale, to deal with carbide flue dust, as it is much more obnoxious than the flue gases themselves. Dust collecting chambers with air or gas filters soon become useless, and neither washing with water nor electrostatic dust collectors have

[1] See also *Schweiz. Chem. Ztg.*, 1919, Nos. 29/30 ; *Chem. Zentralbl.*, 1920, ii., 276.
[2] *Zeitsch. f. angew. Chem.*, 1919, ii., 314.

been fully successful. For small plants and furnaces running at a comparatively small load, the method of the Lonza works at Thusis, Switzerland, is the one most to be recommended. The dust-removing plant at Thusis is said to have worked very satisfactorily since the summer of 1919.[1] The fumes from the carbide furnaces are passed through an atomised water spray and led into a chimney. The plant is constructed in a special manner, in order to ensure contact between the dust particles and the water spray of so intimate a character that the dust is almost completely precipitated. Only a little quite transparent smoke and steam leave the chimney, whilst the water is discharged fully charged with dust. The amount of water used is rather considerable, and, moreover, the treatment of the effluent would require considerable settling tanks in more closely populated districts. Attempts have also been made to remove the dust from the gases in coke towers sprinkled with water,[2] and Kubierschky columns have also been proposed for the purpose.[3]

These arrangements suffer from the same disadvantages as the very efficient centrifugal gas washers of E. Theissen (Munich), Maschinenfabrik Zschocke (Kaiserslautern), and others. The very large quantities of admixed foreign matter rapidly and frequently cause stoppage of all these contrivances, unless large dust chambers are interposed. The separated masses of dust may under circumstances unite with water to form hard cement-like crusts, which are very difficult to remove. So called thermal filters are recommended by W. D. Bancroft.[4] It would be impossible, within the confines of this book, to describe all the arrangements which have been proposed for the purpose of purifying gases and removing dust from them. We may refer, on this matter, to the "Fortschrittsberichte über anorganische Grossindustrie, etc." ("Reports on Progress in the Inorganic Heavy Chemical Industry") and on plant which were published in *Chem. Ztg.*, 1915, No. 118, and 1919, No. 59. Contributions to this important question are also to be found in A. v. Jhering, "Maschinenkunde für Chemiker" (Leipzig, 1906), pp. 298–303; C. Naske, "Zerkleinerungsvorrichtungen und Mahlanlagen" (Leipzig, 1911), pp. 168–184; H. Rabe, "Entnebelungseinrichtungen" ("Removal of Fog"); H. Rabe "Entstaubungsanlagen" ("Dust Removal Plant"), in F. Ullmann's "Encyclopaedia," vol. iv., pp. 562, 564; H. Rabe, "Gas Filters" and "Gas Purifiers," in Ullmann's "Encyclopædia," vol. vi., pp. 1, 25, 26. In the last-mentioned article, on p. 27, a Theissen counter-current washer on the disintegrator

[1] *Umschau*, 1919, p. 236.
[2] See Schlapfer, *loc. cit.*
[3] *Chem. Ztg.*, 1917, *Chem. Techn. Übers*, p. 54; British Patent 7958/1913.
[4] *Chem. Zentralbl.*, 1920, iv., 554.

principle is depicted. The principle of the electrostatic removal of dust from gases by the Cottrell and other systems depends on passing the gases to be purified through a cylindrical space, along the axis of which a wire electrode net is suspended, through which high tension direct current is passed at a voltage up to 100,000 volts. The counter-electrode is formed by the walls of the cylindrical gas chamber. Under the electrostatic action of the current the dust particles settle on the walls of the outer cylindrical chamber, and the dust-free gases escape at the other end of the tube. The method has proved very successful for the removal of flue dust from smelting works, more particularly in America. It appears, however, that it is incapable of dealing with the enormous quantities of carbide flue dust, at any rate in its original form. The fact that in this case the material is highly alkaline may be of some influence. The current consumption is fairly high. In his article on lead,[1] E. Bahlsen gives drawings and references to the literature of the Cottrell [2] system which has quite recently been discussed in detail by O. Johannsen.[3] The further development of electrostatic methods of dust removal has been the object of the following recent German patents by Siemens-Schuckertwerke G.m.b.H., of Siemensstadt, near Berlin, and of other inventors: German Patents 312,049, 314,014, 314,030, 314,171, 314,626, 314,775, 314,947, 315,534, 315,931, 316,498, 316,703, 316,790, 318,432, 318,433, 318,896 and 322,188. The following German patents deal with non-electrical methods.[4] 291,714, 303,831, 306,853, 307,579, 307,890, 313,026, 313,127, 314,170, 314,259, 316,901, 319,936 and 324,443.

Methods of dust removal are also of importance for the purification of blast-furnace gases. In this field mechanical methods predominate, as may be gathered from the articles of O. Johannsen [5] already referred to. The Cottrell process, which, according to O. Johannsen, was based on the experiments of Hohlfeld in Leipzig (1814) and of Oliver Lodge in London and Wales (1854), has achieved no success in Germany, although it has been energetically developed in America in connection with the production of potash from blast-furnace and cement-kiln flue dust. The first firm to replace the older process of removing dust from blast-furnace gases, by washing towers and cyclone washers, by dry filtration with filter cloths

[1] Ullmann's "Encyclopaedia," vol ii., p. 644, see also preceding and following pages.
[2] See also the above-mentioned reports on progress in the *Chem. Ztg.*, 1915, 1919.
[3] *Umschau*, 1920, p 399; *Chem. Zentralbl*, 1919, ii, 912; iv., 68, 445, 1013; 1920, ii., 663, 775. *Zeitsch f. angew. Chem.*, 1920, i, 99. *Stahl. u. Eisen*, 1919, pp. 1377, 1423, 1511, 1546.
[4] See also *Chem Ztg*, 1919, p. 805.
[5] *Umschau*, 1919, p. 583.

was the Halbergerhütte, in the Saar, which, jointly with the firm of Beth, of Lübeck, has introduced a method of filtration of blast-furnace gases which is largely used to-day. Kenneth M. Chance gives the following analysis of a typical Halberg-Beth flue dust [1] :—

Soluble in Water.		Soluble in Hydrochloric Acid.		Additional.	
KCN	5·58	Fe_3O_4	11·68	SiO_2	8·91
K_2CO_3	14·66	ZnS	2·23	C	2·18
$KHCO_3$	23·23	$CaCO_3$	10·39		
$KCNS$	Trace	MgO	1·05		
K_2SO_4	1·13				
$KHCO_2$	3·66				
KCl	10·90				
Na_2CO_3	3·97				
$Fe(CN)_2$	0·48				
$ZnS + PbS$	0·36				

In reference to the partial failure of the Cottrell method when applied to the purification of blast-furnace flue gases, the fact is suggestive that in this case, as in that of carbide flue gases, acid constituents are lacking. The unsatisfactory working of the electrostatic plant in the carbide industry may, therefore, be due to definite unsuitability of the process for such gases. The satisfactory removal of dust from the flue gases is of great importance for the future of the carbide industry, for the gases from the closed ovens can only be burnt and utilised without difficulty if sufficiently free from dust. The complete solution of the problem of dust removal is also very important from a hygienic standpoint and for other reasons, such as the damage which is caused to vegetation.

The endeavour, which was so marked during the War, to utilise all by-products as far as possible directed attention to the residue from the production of acetylene, the so-called carbide sludge. Although this material is unsuitable as a fertiliser, experiments show that it can very well be used as a constituent of mortar. Experiments carried out by K. Schumann and G. Hartmann on behalf of the Bavarian Industrial Institute in 1917, gave such favourable results [2] that the Nürnberg Town Council authorised and recommended the use of carbide sludge for the preparation of mortar.

The manufacture of calcium cyanamide [3] is carried out technically by two methods, mainly that of A. Frank, N. Caro and their associates, and to a lesser extent by the method of Polzenius. In German patent 163,320, Polzenius describes the addition of calcium chloride to the carbide in order to lower the temperature of nitro-

[1] *Chem. Zentralbl.*, 1919, II., 910.
[2] *Sudd Ind Blatt.*, 1920, p. 646.
[3] See F. Muhlert, *loc. cit.*, p. 204.

remain for at least 24 hours. The iron cage is so firmly attached to some portions of the cyanamide that strong hammering or powerful pressure is required in order to loosen the charge; at other points the paper linings serve as a useful separating and insulating medium, and the cyanamide can be readily removed. The wear and tear of the cages may be quite considerable. It is increased by the fact that the sheet iron undergoes serious chemical changes through the action of the heat, the nitrogen, and the carbon, and becomes brittle in course of time. The large and extremely hard lumps of cyanamide are disintegrated by means which will be described later.

There are very few publications on the nature of the technical nitrogenation process. It is known from the patents that the fixation of nitrogen takes place at 700° to 800° C. in the case of barium carbide, and at 1,000° to 1,100° C. with calcium carbide. Also that when the barium compound is used, the reaction is predominantly—

$$BaC_2 + N_2 = Ba(CN)_2$$

and with calcium carbide—

$$CaC_2 + N_2 = CaCN_2 + C.$$

Occasionally the formation of paracyanogen $(C_2N_2)_n$, is observed as a dark amorphous mass which is converted into dicyanogen on further heating, and dissolves in caustic potash to form potassium cyanate; this fact renders it probable that at any rate under certain conditions, apart from the main reaction, the nitrogenation of the carbide takes place in two stages:—

$$CaC_2 + N_2 = Ca(CN)_2$$
$$Ca(CN)_2 + N = CaCN_2 + CN.$$

According to N. Caro [1] the reaction is reversible at 1,360° C., so that the temperature range within which the nitrogen furnace operates most favourably is comparatively small. The optimum temperature within the somewhat narrow reaction range is probably 1,100° to 1,200° C.

Numerous other patents are concerned with the development of the above-described methods which we have only been able to sketch in general terms. Particular attention has been paid to the addition to the carbide charge of such materials as will favour the reaction, reduce superheating, and prevent caking. German patent 212,706 claims the addition of fluorides. In German patents 203,308, 227,854 and 228,925, the Cyanidgesellschaft m.b.H., Berlin, describes the addition to the carbide of a small amount of previously produced calcium cyanamide, as this considerably increases the absorptive

[1] *Zeitsch. f. angew. Chem.*, 1909, p. 170; *Chem. Ztg.*, 1911, "Repertorium," p. 32.

capacity of the carbide for nitrogen. According to the description in the patent, 100 kg. of carbide are mixed, for example, with 10 kg. of powdered calcium cyanamide ; from this mixture a product containing 20 to 24 per cent. of nitrogen is obtained very rapidly at 900° C. The amount of such additions is naturally dependent in practice on the quality of the carbide which is used. German patent 258,342 of the Stickstoffwerke G.m.b.H., Berlin, and the Bayrischen Stickstoffwerke, claims the use of a porous layer surrounding the carbide, in order to obtain an especially uniform product. In German patent 309,173, P. Dienemann claims a special method of working, in order to reduce the wear and tear of the cages.

According to N. Caro,[1] the composition of crude cyanamide is :—

52	per cent.	$CaCN_2$
21	,,	CaO
14	,,	C
2	,,	SiO_2
4	,,	iron oxide, alumina, etc.

In U.S. patent 1,155,797 the following analysis is given :—

57	per cent.	$CaCN_2$
3	,,	CaC_2
18	,,	CaO
12	,,	free C
5	,,	$CaCO_3$
5	,,	various impurities, such as iron oxide, alumina, silica, etc.

The following analysis is given in the description of the Muscle Shoals [2] plant :—

63	per cent.	$CaCN_2$
2	,,	CaC_2
13	,,	CaO
1	,,	CaS
11	,,	free C
3	,,	SiO_2
2	,,	MgO
2	,,	$Fe_2O_3 + Al_2O_3$
3	,,	various impurities.

The composition of the product varies naturally with the character of the raw materials. It is always characterised, however, by a relatively large amount of non-nitrogenated carbide, amounting on

[1] *Chem. Met. Eng.*, 1919, p. 8.
[2] *Chem. Ztg.*, 1911, "Repertorium," p. 32.

the average to about 1·5 per cent., but which may be as high as 2 to 3 per cent. The removal of this carbide will be referred to below. In fresh cyanamide the nitrogen is practically all present in the form of calcium cyanamide, $CaCN_2$, which when pure, contains 35 per cent. of nitrogen. Thus the three samples of calcium cyanamide, the analysis of which has been given above, contained 18·20, 19·25, and 22·05 per cent. of nitrogen respectively.

Apart from the above-mentioned articles, there are various articles by A. Frank and by N. Caro [1] which give comprehensive descriptions of the methods used. Latterly E. O. Siebner has given a short summary in the *Umschau* [2] of the Frank-Caro process, which contains two views of the Trostberg Works. Siebner gives the following figures for the annual output capacity of the three large Frank-Caro works in Germany for 1920 :—

	Tons of Nitrogen.
Piesteritz Works	35,000
Chorzow Works	20,000
Trostberg Works	16,000
Total	71,000

The total output of nitrogen in the form of calcium cyanamide produced in Germany is 100,000 to 110,000 tons. The remaining 30,000 to 40,000 tons of nitrogen are produced by the works at Knapsack and Gross Kayna with a joint output capacity of 28,000 tons of nitrogen, and by the Lonza Works at Waldshut with an output capacity of 12,000 tons.

In a series of articles on the rational utilisation of fuel,[3] there are included contributions by N. Caro and E. R. Besemfelder on the fuel necessary for the production of calcium carbide, which are of great importance in ascertaining the production cost. N. Caro [4] gives the following figures on the fuel and power requirements per kilogram of fixed nitrogen :—

2·5 kg. coke,
17·0 kg. pulverised coal,
or approximately 1 kg. of ordinary coal if the electric power is supplied by water power.

In the course of a controversy which ensued, N. Caro corrected these figures to :—

[1] *Zeitsch. f. angew. Chem.*, 1906, p. 1569; *Chem. Ztg.*, 1903, p. 513; 1905, p. 1046; 1906, p. 449.
[2] *Chem. Ztg.*, 1920, p. 488.
[3] *Ibid.*, 1915, 1916, 1917, 1918, 1919.
[4] *Ibid.*, 1919, p. 282.

3·3 kg. of coke,

or {2·5 kg. of coke, and
0·9 to 1 kg. of coal,[1] apart from electric power.

He also stated that these quantities could be reduced to 2·8 kg. of coke if the installations were perfectly equipped.[2]

In a pamphlet "Aus Luft durch Kohle zum Stickstoffdünger" ("Nitrogenous Fertilisers from the Air by Means of Coal") (Berlin, 1920), he estimates the total amount of fuel per kilogram of nitrogen in calcium cyanamide at 3·5 kg. when the necessary electric power—namely, 15 to 17 k.w.h. per kilogram of nitrogen—is supplied by water power.

E. R. Besemfelder,[3] on the other hand, gives the following estimate, which he bases on actual works figures :—

Fuel used per Kilogram of Nitrogen in Calcium Cyanamide.

2·740 kg. of coke for the production of carbide.
0·220 kg. of electrode carbons for production of carbide.
1·200 kg. of coal for the manufacture of quicklime for the production of carbide.
0·015 kg. of electrode carbon for nitrogenation.
0·170 kg. of tar oil for dust prevention in the calcium cyanamide.
0·075 kg. of coke and briquettes for drying the fluorspar and for the production of CO_2.

Total 4·420 kg. of fuel and 15·9 k.w.h.

M. Novak[4] utilises the figures of both Caro and Besemfelder, and estimates 5·055 kg. of fuel per kilogram of nitrogen in cyanamide. As the conditions naturally vary, one may assume an average of 3·5 to 4 kg. of fuel and 16 k.w.h. per kilogram of fixed nitrogen.

We have already mentioned that various additions are made when nitrogenating carbide, in order to promote the reaction. Originally, about 10 per cent. of finely ground fluorspar was ordinarily added.[5] In Germany and other countries, however, the addition of fluorspar[6] has largely been abandoned. At Ljunga they still use it, whilst at Alby they do not.[7] M. Novak[8] writes as follows : "There are special

[1] *Chem. Ztg.*, 1919, pp. 604, 865.
[2] *Ibid.*, 1919, p. 604.
[3] *Ibid.*, 1919, p. 521–522.
[4] *Ibid.*, 1919, p. 865.
[5] H. Goldschmidt, *Zeitsch. d. Ver. Deutsch. Ing.*, 1919, pp. 877 *et seq.* ; F. Carlson, *Chem. Ztg.*, 1906, p. 1261.
[6] *Chem. Ztg.*, 1912, p. 1293, 1913, p. 143.
[7] N. Caro, *Chem. Ztg.*, 1919, p. 604.
[8] *Chem. Ztg.*, 1919, p. 865.

reasons for the abandonment of the use of fluorspar. Fluorspar was used in Trostberg for the manufacture of cyanamide until 1917, at which time the railways were not so overburdened and freights were cheaper. The addition of fluorspar and other similar substances was entirely justified,[1] as at Trostberg a cyanamide was manufactured containing 19·5 to 20 per cent. of nitrogen. The necessary apparatus and machines for the utilisation of fluorspar were also acquired in 1915 for the works at Piesteritz and Chorzow, but the carbide furnaces which were there employed produced a carbide of such quality that dilution with fluorspar could not be contemplated." In any case the cyanamide industry could manage quite well without fluorspar.

The amount of current required for heating up the nitrogenation furnaces is low, on account of the small specific heat of carbide (see the description of the American works at Muscle Shoals, pp. 402–6). Many attempts have been made to ensure better heat and power economy in the whole process, which comprises two difficult grinding operations—namely, that of the carbide before nitrogenation and of the crude cyanamide, and the heat balance of which is by no means ideal. The hot carbide from the furnace radiates its large heat contents uselessly into the air of the cooling shed, and is reheated to 1,000° to 1,200° C. in the nitrogenation furnace. The manufactured cyanamide loses this heat uselessly after nitrogenation, and must finally be reheated to 100° to 200° C. in order to be converted into ammonia.

A remedy was for some time supposed to have been found for the last-mentioned loss by decomposing the unbroken hot product of the nitrogenation furnaces directly with water or steam in large lumps. Attempts have also been made to utilise the temperature of the carbide which is discharged from the furnace. Erlwein's old suggestion to heat lime and carbon in electric resistance furnaces with carbon electrodes and to blow nitrogen through the highly heated mass, was realised by Siemens and Halske.[2] As carbide manufacture improved the method became quite uneconomical, and, moreover, it never yielded a high grade cyanamide; the product which was obtained never contained more than 12 to 14 per cent. of nitrogen. When one considers that carbide formation only takes place at about 1,600° C., that nitrogenation is most rapid at 1,100° to 1,200° C., and is reversible at 1,360° C., it will be clear how extremely difficult it is, suitably to combine both reactions. Erlwein's idea was, however, once more renewed in U.S. patent 1,021,445 of

[1] *Zeitsch. f. Elektrochemie*, 1907, pp. 69, 101, 605.
[2] *Zeitsch. f. angew. Chem.*, 1903, p. 535; *Zeitsch. f. Electrochemie*, 1906, pp. 551, 665.

A. Bonnington and G. Ackers. According to German patent 242,989, substances promoting the reaction, such as calcium chloride or calcium fluoride, are added to the carbide whilst still molten; the mass is then allowed to cool slightly and whilst still red hot is treated with nitrogen in a suitably constructed mill. According to C. Krauss [1] this process has not yet emerged from the experimental stage, as the grinding of the red-hot carbide involves great technical difficulties. If red-hot furnace carbide is to be treated, exact control of the temperature of tapping is an absolute necessity; the slowness of the absorption of nitrogen by the carbide would be a difficulty. The process described in M. Zöllenkopf (German patent 293,258) might also be applied under definite conditions to tapped carbide. This patent utilises the property of molten basic slag of dissolving carbide; a mixture of the two substances is allowed to cool and is passed at a suitable temperature into a mill, through the hollow axle of which nitrogen is introduced under pressure. The sensible heat of the melt is used, and a calcium phosphate containing cyanamide is so obtained. The Frank-Caro process uses small nitrogenation furnaces, and at an early date attention was directed to the provision of better apparatus which would allow continuous nitrogenation. In a modern plant with an output of 400 to 450 tons of cyanamide daily, the number of the nitrogenation furnaces is very considerable and averages about 700 to 1,000. There are many reasons, based on the whole development of modern technology, against discontinuous operation of small units; but the Frank-Caro apparatus appears to be very suitable for nitrogenating carbide, owing to peculiarities of the material and of the reaction. The advocates of a continuous process have so far not been able to point to similar success and the wide distribution of the Frank-Caro system indicates its suitability for the purpose. That it is capable of improvement and that a perfectly continuous process which utilises the sensible heat of the furnace carbide still remains a desirable achievement, would not be disputed by anybody for a moment. But Goethe's much-disputed statement that "all theory is grey" is fully true in this case.

The Polzenius system represents a semi-continuous process. In his fundamental German patent 163,320, Polzenius shows that the nitrogenation of metallic carbides can be considerably promoted by the addition of chlorides of the alkali, alkaline earth, or other metals. He succeeded in obtaining 100 gm. of a product containing 19.3 per cent. of nitrogen at 700° to 800° C. from a mixture of 62 gm. of calcium carbide and 18·7 gm. of calcium chloride, the absorption of nitrogen being exceptionally active. He first called

[1] Ullmann's "Encyclopædia," vol. iii., p. 214.

this product "Stickstoffkalk" (nitro-lime). The Gesellschaft für Stickstoffdünger G.m.b.H., of Westeregeln, near Magdeburg, carried out the first experiments on the Polzenius process on the property of the Consolidirten Alkaliwerke and developed it further, as described in German patent 242,989. They were the first German works to place synthetic cyanamide on the market in 1905.

Publications on the use of such catalytic additions to carbide before nitrogenation, including fluorspar, have been made by Kühling,[1] Polzenius,[2] Bredig,[3] Foerster and Jacoby,[4] Rudolfi,[5] and Pallacci.[6]

The experimental works at Westeregeln were soon dismantled, and the Gesellschaft für Stickstoffdünger was absorbed by the A.G. für Stickstoffdünger at Knapsack (near Cologne), a director of which company, C. Krauss, has described the Polzenius process fully.[7] His process is also used by the Mitteldeutsche Stickstoffwerke Gr. Kayna, near Merseburg, by the Lonza Works at Basle, and in other places, but this process is not nearly so widely used as the Frank-Caro process (see the above output figures). According to Krauss, calcium carbide is mixed with 10 per cent. of its weight of strongly calcined calcium chloride in ball or tube mills, and very finely ground. The mills are filled with nitrogen, in order to avoid danger of explosion. The finished Polzenius mixture is filled into iron boxes about 30 cm. high, which are easily dismantled and which have perforated floors; these replace the Frank-Caro nitrogenation cages. The boxes are superposed on iron carriages and introduced into a tunnel furnace (German patents 282,213, 285,699; French patent 464,750). The tunnel furnace comprises four sections, as shown in Fig. 9. In the pre-heating section the Polzenius mixture is warmed by the hot furnace gases, in the heating zone it acquires the necessary reaction temperature, in the reaction zone nitrogenation takes place and in the cooling zone the finished product is so far cooled that it can conveniently be removed and passed on for further treatment. The stream of nitrogen passes in the opposite direction to the solid material, so that heat exchange occurs. The nitrogen is pre-heated in the cooling zone, and the hot gases, consisting of excess of nitrogen, acetylene, argon, and so forth, transfer the greater part of their heat contents to the cold Polzenius mixture in the pre-heating zone. The heating in the so-called heating zone takes place largely with

[1] *Ber.*, 1907, p. 310.
[2] *Chem. Ztg.*, 31, 958.
[3] *Zeitsch. f. Elektrochemie*, **13**, 69, 605.
[4] *Ibid.*, **13**, 101, 820.
[5] *Zeitsch. f. anorg. Chem.*, 1907, p. 170.
[6] *Zeitsch. f. Elektrochemie*, **14**, 565.
[7] Ullmann's "Encyclopædia," *loc. cit.*, vol. iii., p. 210.

the help of the very hot gases from the reaction zone. Very little fuel or power is therefore required for external heating by direct firing or by electricity. The heating chamber serves essentially as a heat regulating device. In the reaction zone there is a heat exchange between the cold gases which enter, the pre-heated gases from the cooling chamber and the hot Polzenius mixture, so that attainment by the latter of the optimum temperature for nitrogenation is assured.

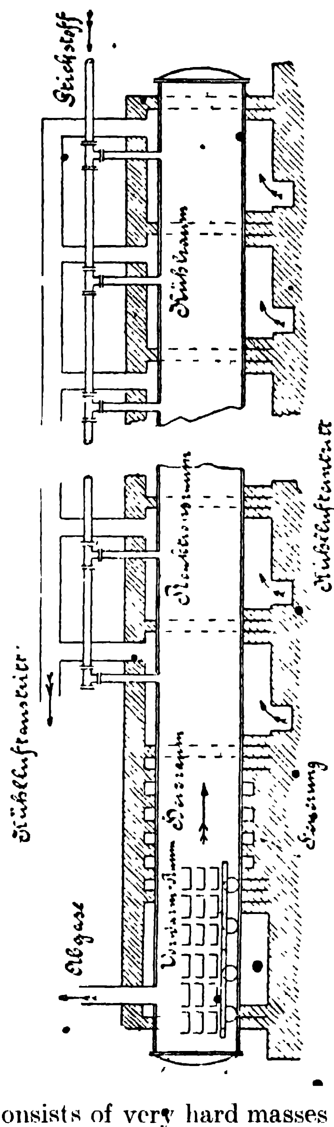


FIG. 9.

Abgase = Flue gases. Vorwarm Raum = Preheater. Reaktionsraum = Reaction chamber.
Heizraum = Heating chamber. Kuhlraum = Cooling chamber. Feuerung = Fire gases.
Stickstoff = Nitrogen. Kuhlluftaustritt = Outlet for cooling air. Kuhllufteintritt = Inlet for cooling ai

A very large excess of cold nitrogen would be required were it necessary to regulate the furnace temperature by this means alone. The furnace is, therefore, surrounded by an outer cooling chamber, and the internal wall is built of heat-conducting material. If the temperature recorders show a dangerous rise of temperature inside the furnace, cool air or other gases can at once be passed into the cooling chamber, in order to lower the temperature. The intake of nitrogen is so arranged that it can be distributed by branch conduits through the whole reaction and cooling zones of the furnace, and that any local overheating can quickly be prevented by opening the corresponding gas connections.

The nitro-lime (calcium cyanamide) which is obtained consists of very hard masses weighing 100 kg. and over, according to the size of the containers. Under normal conditions the reaction product contains 0·25 per cent. of carbide only, a quantity which is only increased if the furnace is too cold or too hot, or if there was a deficiency of nitrogen. The

heated to such a temperature that nitrogen is rapidly absorbed. The cars then slide rapidly away from the reaction zone down the slope, 8, so that all overheating is avoided, and are removed through 9, by rollers, 10. According to Thrane, the nitrogenation temperature is between 900° and 1,300° C. In German pat. 312,088 he describes a ring-furnace suitable for the nitrogenation process, in which a ring-shaped plate running on rollers carries the carbide to be nitrogenated, supported on a layer of inert material, preferably finished calcium cyanamide. The furnace is heated electrically. The nitrogen passes continuously in an opposite direction to the revolving ring plate, from which the finished nitrogenated product is removed by a mechanically actuated knife. According to German pats. 305,061 and 305,532 by M. Novak, nitrogenating chambers carried on trucks with internal electric heating are passed through a tunnel-furnace, so that his arrangement is more or less a com-

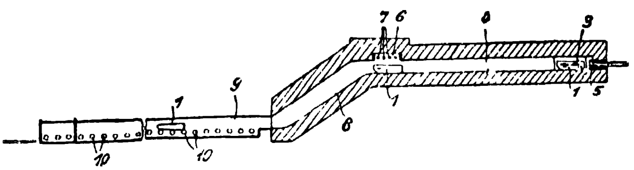


FIG. 10.

promise between the Frank-Caro and the Polzenius systems. In German patent 312,934 by the Elektrizitätswerke Lonza, of Basle, a rotary furnace is described in which the excess of nitrogen is circulated over heating or cooling arrangements outside the furnace, to which it then returns. In this manner the reaction temperature is maintained at a constant level and the heat economy is very good. It is said that at the Lonza Works these or similar furnaces are used with satisfactory results.

The principle described by Tofani (German patent 246,077) reappears in German patent 314,363 by Det Norske Aktieselskab for Elektrokemisk Industri and Norsk Industri-Hypotekbank, of Kristiania, and consists in conveying carbide dust into the furnace by a nitrogen blast and initiating the heating by an arc. According to German patent 318,286 by Karl. Prinz zu Löwenstein, and F. Hauff, methane is first decomposed, by heat, into hydrogen and carbon. The hydrogen is burnt with air, and nitrogen is thus obtained, whilst the carbon, according to their statement, is exceptionally suitable for the manufacture of nitrogen absorption mixtures from barium carbonate or lime and carbon. The patent thus represents a transition to the cyanide processes which we will discuss later. The

reaction masses are briquetted and treated with nitrogen in a rotary furnace. Cyanides and cyanamides are said to be formed at 1,200° to 1,400° C. According to German patent 319,798, A. Lang blows carbide dust into the furnace in a current of nitrogen, but he does not heat the mixture. The necessary temperature is attained by pre-heating the nitrogen to a sufficiently high temperature. The Compagnie d'électricité Industrielle are erecting a continuous furnace for the production of 20 to 30 tons of cyanamide daily in their Marignac Works.[1]

J. H. Lidholm and the Dettifoss Power Co., Ltd., of London,[2] propose to introduce nitrogen and carbide into a rotary drum furnace from opposite ends, thus attaining a satisfactory transference of heat. Their process is characterised by the fact that the nitrogen is introduced at a pressure [3] of 5 to 10 atmospheres, and is utilised to rotate the furnace (German patent 312,618, French pats. 469,045, 469,046). In order to avoid sintering, carbide of 55 to 60 per cent. strength only is used, or an inert substance such as sand is mixed with carbide of higher quality. It has been found that for each pressure of the nitrogen there is a definite degree of dilution which must be continuously maintained, and is easily ascertained by experiment. At an excess pressure of 1 atmosphere, a 60 per cent. carbide mixture yields a cyanamide containing 20 per cent. of nitrogen, and the loss of nitrogen amounts to 20 per cent. only of the whole quantity used. In French patent 469,046, British patent 28,524/1913 and German patent 274,472, which describe a slightly different method, the patentees maintain that nitrogenation occurs instantaneously at 1,500° C., and that the best method of nitrogenation is to pass carbide dust into nitrogen gas at 2,000° C. This statement is at variance with all other experience. In German patent 325,152 the A.B. Nitrogenium describes a stirrer for cyanamide furnaces.

The comments of C. Krauss [4] on the proposals of German patent 254,015 by G. Scialoja naturally also apply to U.S. patent 1,126,000 of Tuneichi Fukiyama, Tokio, according to which the reaction temperature is attained by burning a portion of the carbide in air, the residual nitrogen of which is utilised for nitrogenation. A resistance furnace to operate at reduced pressure is described by L. G. Patrouilleau in French patent 475,195. In U.S. patent 1,123,763, H. W. Lamb describes the production of iron carbide, FeC_2, from iron oxide and coke, coal or pitch; this is said completely to absorb nitrogen at a high temperature, forming nitrides

[1] *Chem. Ztg.*, 1921, p. 188.
[2] See also C. Krauss, *loc. cit.*
[3] *Metallbörse*, 1920, p. 1202.
[4] *Loc. cit.*

and similar substances which can be decomposed by steam with formation of iron carbonate and ammonia. In French patent 456,826 Barzano and Zanardo claim the preparation of powdered cyanamide directly in the nitrogenation furnace. Other patents dealing with the cyanamide industry or with kindred questions are German patent 149,594 of the Ampère Electrochemical Company, German patents 200,986 and 235,662 of the B.A.S.F., and U.S. patent 982,288.

The product obtained by the Polzenius process is distinguished from the Frank-Caro cyanamide by containing chlorine. C. Krauss [1] gives the following analyses of the two materials :—

Calcium Cyanamide

	Polzenius Product. Per cent.	Frank-Caro Product. Per cent.
N	about 20 to 21	20 to 21
C	" 17	17 " 18
Cl	" 5	—
CaO	" 54	56 " 57

Apart from those already mentioned, we may refer to the following theoretical articles : O. Kühling and O. Berkold,[2] M. Le Blanc and M. Eschmann,[3] G. Erlwein, C. Warth and R. Beutner,[4] J. Pranke,[5] E. J. Briner and A. Kühne,[6] G. Bredig [7] and P. Dolch.[8]

The further treatment of both Frank-Caro and Polzenius cyanamide is the same. The cages or boxes are first allowed to cool and are then emptied. The large lumps of crude material are usually coarsely crushed in rock-breakers and then finely ground in ball mills. The construction of the mills is only very slightly different from those employed in cement works. The engineering works, Gebr. Pfropfe, of Hildesheim, recommend their Quadruplar mills for grinding cyanamide, and the Siemens Schuckert-Werke G.m.b.H., of Siemensstadt, near Berlin, have patented a special crusher for the purpose (German patent 316,605). Both cyanamide mills and carbide mills must be filled with inert gas if explosions caused by the more or less considerable quantity of carbide are to be avoided. Flue gases are frequently utilised instead of pure nitrogen for this purpose ; as they essentially consist of carbon dioxide and nitrogen they contain practically no oxygen.

[1] *Loc cit.*
[2] *Chem. Ztg.*, 1908, Repert., 109 ; 1909, Repert., 109.
[3] *Ibid.*, 1911, Repert., 151.
[4] *Ibid.*, 1911, Repert., 180.
[5] *Ibid.*, 1913, Repert., 333, 503.
[6] *Ibid.*, 1913, p. 665.
[7] *Ibid.*, 1913, p. 831.
[8] *Zeitsch. f. Elektrochemie*, 1920, p. 455.

The very dusty, crude cyanamide flour which is finally obtained, is seldom directly suitable for further utilisation or for sale. The product of the Frank-Caro furnaces sometimes contains 2 to 3 per cent. of carbide, and that from the Polzenius process at least 0·25 per cent.; in the case of any irregularity these figures may be considerably higher. This carbide forms acetylene with the moisture in the atmosphere during loading and storing, and this may explode through spontaneous ignition or other causes. A serious explosion actually occurred on the Norwegian steamer *Snorre*. A law was then passed in Norway reducing the permissible contents of carbide in cyanamide to 0·2 per cent. E. Simonsen [1] states that this figure is too high, and is in favour of a regulation permitting the transport of cyanamide in sheet-iron drums only, such as are used for carbide. According to Simonsen, his explosion method of testing is better than that of Caro. Simonsen's method is to stir 20 gm. of material with 10 c.c. of water in a 250 c.c. flask; after standing for two hours, the gas should not be capable of being exploded by the flame of a match. Caro's method consists in liberating the acetylene with saturated brine, collecting the gas over brine and determining the final volume after waiting for fifteen minutes. Simonsen considers the determination of the acetylene by cuprous chloride solution to be entirely unsatisfactory.

Some "degasification" of the cyanamide occurs in the cooling chambers and mills, but not enough to reduce the carbide contents sufficiently. For this purpose so-called hydro-mixers are used, which usually consist of double-walled drums into which water is sprayed through jets, whilst the powdered cyanamide is passed through the drum by a screw conveyor. If necessary, such degasification drums can be arranged in series so that the material is certain to leave the apparatus with a very small amount of carbide only. The addition of water through the spraying jet can be regulated, and is altered according to the carbide contents of the cyanamide. Considerable quantities of heat are released by the reaction:—

$$CaC_2 + 2H_2O \quad Ca(OH)_2 + C_2H_2.$$

On hydration with 20 to 50 times the theoretical amount of water, each gram of carbide develops an average of 406 cals. when the carbide is in large pieces and of 377 cals. when in small lumps of 1 to 5 gm. weight. 1 gm. of pure carbide develops 414·6 cals.[2] This heat must be removed from the hydro-mixers if serious alterations in the calcium cyanamide, more particularly the formation of dicyandiamide and the liberation of ammonia, are to be avoided.

[1] *Chem. Ztg.*, 1915, p. 123.

[2] J. H. Vogel, "Das Acetylen," Leipzig, 1911, p. 8?.

The double wall of the drum is therefore used for effective cooling, or single-walled drums are used, the outsides of which are sprayed with cooling water. Hydro-mixers, which may also consist of open or covered troughs, are supplied by the Engineering Works, Gebr. Pfropfe, Hildesheim, and others. In the American plant at Muscle Shoals,[1] these troughs are 0·91 m. wide and 11 m. long. They are open and contain a shaft which makes 50 revolutions per minute, and contains stirring arms 408 mm. long. A quantity of water, corresponding to the carbide contents, is sprayed on to the trough. The cyanamide passes through the apparatus at a rate of 15 m. per minute, becomes slightly warm, and leaves in a perfectly dry condition. The liberated acetylene is lost.

The A.G. für Stickstoffdünger, at Knapsack, near Cologne, brings the cyanamide into contact with a definite quantity of steam (German patent 260,469, French Patent 450,435). In this case the regulation of the temperature is still more difficult. According to French patent 456,765, F. W. MacMahon stirs up the cyanamide with 30 to 40 per cent. of water with effective cooling. This quantity of water appears to be very high under normal conditions; it would probably lead to the formation of lumps and reduce the nitrogen contents of the final product to a very low figure by the addition of so much excess.

The degasified cyanamide sometimes undergoes a further mixing process in order to reduce the nitrogen content to a standard figure or in order to oil it. For the first purpose, poor qualities are mixed with good qualities, or inert materials are added; for the latter purpose, 3 to 4 per cent. of heavy tar oil is added in order to diminish the dustiness. G. Zarniko proposes to carry out the degasification, mixing and oiling in one process, by using a slaking mill with water spray, the mill being filled, as usual, with an inert gas. The required liquid is sprayed in through the same opening as the cyanamide. The material is intimately mixed by special rakes inside the mixing drum, and is sifted through a cylindrical grating before discharge (German patent 294,993). Kenneth F. Cooper and the American Cyanamide Company, of Nashville (Tennessee), treat a raw material containing 3 per cent. of carbide in a rotary cooling cylinder with 10 to 15 per cent. by weight of water, to which some oil or other suitable binding material is added. The acetylene escapes, and perfectly dry, degasified and dust-free cyanamide can be discharged from the drum (U.S. patent 1,155,797).

Calcium cyanamide is characterised by being very dusty. For hygienic reasons many attempts have been made to remove this

[1] *Chem. and Metall. Eng.*, 1919, pp. 8 *et seq.*

objectionable quality, so that the product may be more useful to the farmer. On April 1st, 1915, the Prussian Minister of Agriculture, Domains, and Forests instituted a prize competition for answers to the following two questions :—[1]

(1) What action has calcium cyanamide as a fertiliser when used at various seasons on various soils and in various proportions on various crops ?

(2) How may the spreading qualities of cyanamide be improved ?

The committee for adjudging the answers to question (2) consisted of Ramm of Berlin, Vibrans of Colvörde, Albert of Münchenhof, Günther of Berlin, and N. Caro of Berlin. N. Caro gave a detailed report on the answers to question (2), and on kindred matters in the *Chem. Ztg.*, 1920, pp. 53 *et seq.* In his judgment, he assumed the following average analysis :—

58 to 60	per cent.	calcium cyanamide, $CaCN_2$.
9 ,, 12	,,	free carbon, mainly in the form of graphite.
3 ,, 5	,,	of compounds insoluble in acids, exclusive of carbon.
20 ,, 28	,,	of free lime, CaO.
0·5 ,, 1	,,	of carbide, CaC_2.
0·5 ,, 1	,,	of other constituents.

The dusty and corrosive properties of calcium cyanamide are essentially due to the presence of carbide and free lime. Pure $CaCN_2$ is only slightly corrosive. It decomposes under the influence of moisture, forming monocalcium cyanamide and slaked lime :—

$$2CaCN_2 + 2H_2O = Ca(HCN_2)_2 + Ca(OH)_2.$$

The slaked lime is in a particularly corrosive condition. The property of cyanamide of absorbing moisture and CO_2 is due to its contents of CaC_2 and free lime, and the same ingredients are the cause of increase of volume on storage, with reduction in the nitrogen contents. Calcium cyanamide itself is also hygroscopic.

The earliest proposals for removing the dustiness of cyanamide and rendering it less corrosive depended on simultaneously decomposing the carbide and slaking the lime with water. In order to convert 20 to 28 per cent. of CaO and 0·5 to ? per cent. of CaC_2 into $Ca(OH)_2$ 7 to 10 parts of water must be added to the cyanamide—namely, 6·5 to 9 parts for hydrating the free lime, and 0·5 to 1 part for decomposing the carbide. Unfortunately the method is not successful in practice. It was found that free lime is present in crude cyanamide in the so-called dead burnt condition, and only reacts

[1] *Chem. Ztg.*, 1915, p 301.

with water very slowly. The CaC_2 is decomposed immediately, but the free CaO only forms $Ca(OH)_2$ very gradually, and the latter absorbs further water with formation of complex hydrates. These hydrates gradually part with their water to the free CaO and the $CaCN_2$. All these reactions cause liberation of heat. When treating small quantities of cyanamide with water it is quite possible to disperse the heat by radiation, but when treating large quantities this method appears to be impossible or impracticable. Therefore on storing moistened cyanamide one must reckon with the development of heat of reaction locally and local action of water on calcium cyanamide. In consequence, very prejudicial changes occur, represented by equations (*a*) and (*b*).

$$\begin{aligned}
&(a)\quad 2CaCN_2 + 2H_2O = Ca(HCN_2)_2 + Ca(OH)_2\\
&\quad Ca(HCN_2)_2 + 2H_2O = Ca(OH)_2 + H_2CN_2 \text{ (Free Cyanamide)}\\
&\quad 2H_2CN_2 = (H_2CN_2)_2 \text{ (Dicyandiamide).}\\
&(b)\quad 2CaCN_2 + 2H_2O = Ca(HCN_2)_2 + Ca(OH)_2\\
&\quad Ca(HCN_2)_2 + 5H_2O = CaCO_3 + CO_2 + 4NH_3.
\end{aligned}$$

The dicyandiamide has an injurious effect on the manurial value, and the escaping ammonia causes loss of nitrogen. The numerous proposals which have been made to add water directly to calcium cyanamide, to granulate or compress it in the form of a plastic mass, to add moistened colloids or hygroscopic salts, such as magnesium or calcium chloride, to add peat litter or sulphite-cellulose liquor, all lead to the above-mentioned disadvantages. Of the 125 answers arising out of the above-mentioned prize competition, many consisted of similar suggestions, none of which have been introduced in practice. An American works manufactured cyanamide briquettes according to German patent 321,646 of the Bayrischen Stickstoffwerke without permanent success. Experiments with granulated cyanamide have also been made in Germany, but it was found that a decrease in the fertilising value was produced. According to a communication from Odda,[1] the granulating plant of the North-Western Cyanamide Company at that place had an output capacity of about 350 tons daily. The granulated cyanamide, containing 16 per cent. of nitrogen, was found to be quite good; it contains lime in the slaked condition, and has so little action on seedlings that it can be utilised as a top dressing. It has no injurious action on the skin. The reactions which take place in the soil with ordinary cyanamide, more particularly the formation of ammonia and urea, have already been initiated and facilitated in the new product, so

[1] *Chem. Ztg.*, 1915, p. 320.

that the nitrogen is more quickly absorbed. Comparisons of the degree of subdivision show the following values :—

Meshes per square inch.	Oiled Cyanamide.	Granulated Cyanamide.
14 to 34	26 per cent. ..	63 per cent.
34 ,, 175	30 ,, ..	28 ,,
Dust	44 ,, ..	9 ,,

The North-Western Cyanamide Company also sell cyanamide in the form of dust containing 20 to 21 per cent. of nitrogen, as a weed killer.

A. Stutzer (German patent 242,522) found that certain colloids, such as iron oxide, prevent dusting, and also assist the formation of urea. The most satisfactory process is that of German patent 225,297, which recommends oiling. At present this method is alone used in practice ; the degasified cyanamide is treated with 3 to 4 per cent. of heavy coal-tar oil or paraffin oil in special mixers. Oils containing phenol are injurious, as they form calcium phenolate, which poisons the soil bacteria. The oiled material absorbs water, but with practically no local rise of temperature, does not lose ammonia, and is much less dusty. According to Carlson's German patent 235,754, the free lime is rendered harmless by treatment with carbon dioxide and water. According to German pats. 226,340 and 252,164, Stutzer forms saccharates with molasses, or adds sulphite-cellulose liquor or uses mixtures of cyanamide and calcium nitrate ; the Ostdeutschen Kalkstickstoffwerke utilise dry, finely ground bitumen (German patent 241,995). H. Schröder (German pat. 243,226) recommends magnesium or calcium chloride as an addition, and M. Müller (German patent 262,473) adds sulphite cellulose liquor. According to U.S. pat. 1,042,746, A. P. Zamore and O. F. Carlson fix the dust in cyanamide with nitric acid. According to Norwegian patent 23,064, of Carlson, calcium cyanamide is mixed with so much nitric acid of 3 to 25 per cent. strength that the final product contains 15 to 20 per cent. by weight of the acid. According to Norwegian patent 23,063, of the same inventor, cyanamide is simultaneously treated with water and non-drying oils, or with 0·5 to 10 per cent. of water, 5 to 50 per cent. of carbon dioxide, and 1 to 5 per cent. of certain fats.

In German patent 295,142, F. Winterfeld claims a particularly favourable anti-dusting action by the addition of dolomitic sand. O. Neuss and H. Stiegler mix with peat litter previously soaked in magnesium chloride solution (German patent 298,200). According to German patent 303,079, F. Steimmig adds Glauber salts, whilst, according to German patent 304,965, W. Schwarzenauer adds shale

oil. According to German patent 313,414, Thos. Waage compresses cyanamide with powdered phosphates which are moistened with solutions of potash salts. A suitable press is described by the engineering works, F. Kilian in German patent 300,801. According to U.S. patent 1,098,651, cyanamide is briquetted and then reground. According to U.S. patent 1,135,639, F. S. Washburn proposes to mix 17 parts of cyanamide with 100 parts of slaughter-house offal. French patent 474,882 deals with a granulating process.

Mixtures of cyanamide, basic slag or potash salts, some of which are of poor quality and others rather unstable, are less suited for the industry than for the farmer, who can use them there and then. In Germany, during the War, it was unfortunately scarcely possible to oil cyanamide, on account of lack of suitable raw materials. The addition of tar, of which 15 per cent. was recommended,[1] does not serve equally well.

The addition of acid in order to combine with the free lime appears especially attractive, if the simultaneous action of any excess of water can be avoided or otherwise neutralised. Nitric acid suggests itself at once, as it contains nitrogen and does not therefore lower the nitrogen content of the final product appreciably, if at all. The action of the acid is never confined to the solution of the free lime, but it also acts on the calcium cyanamide, which is thus partially converted into calcium nitrate and into salts of urea or ammonia (see Stutzer, German patent 242,522). The possibility of the formation of calcium humate is referred to in German patent 298,200. Attempts should therefore be made to utilise humic acid, which might be obtained from peat or lignite, by directly mixing the calcium cyanamide in the dry condition with these voluminous substances, which are distinguished by great absorptive capacity. It has also been experimentally established that very dusty powders are considerably altered in their surface properties by being placed between two electrodes in an electric field, that is, if treated as the gases are treated in the Cottrell process. The particles are electrostatically affected and are said not to cause so much dust after being treated by the high tension current. Experiments of this character with calcium cyanamide seem desirable. Experiments will show whether Plauson's colloid mill [2] will prove of value for oiling or homogenising cyanamide together with some other medium such as humic acid.

Much work has been done on the physiological action of cyanamide in consequence of its corrosive and dusty properties. The most

[1] *Umschau*, 1919, p. 192.
[2] *Chem. Ztg.*, 1920, pp. 553, 565.

remarkable are the extraordinary effects which occur when cyanamide dust is inhaled before or after absorption of alcohol, and which manifest themselves in a dark bluish-red coloration of the face and the upper part of the body, shortness of breath, oppression, palpitation, and so forth. The typical symptoms of cyanamide poisoning usually last for one to two hours only, and no further injurious consequences have been observed. The phenomena seem to be definitely connected with those of ordinary cyanogen poisoning, but these latter are much more dangerous. Siebner [1] has written comprehensively on these questions. The comparatively extensive literature has been co-ordinated and summarised by him. The hygiene of the cyanamide industry has also been considered in detail by F. Koelsch.[2] Van Husen [3] describes the various forms of inflammation of the skin caused by cyanamide, and Schlier [4] describes the general interference with health which may occur by handling it.

The changes which cyanamide undergoes when moistened, in order to remove the dusting properties, and also when the degasification process is unsatisfactorily carried out, occasionally lead to serious decomposition on storage by the moisture of the atmosphere. The absorption of water and carbon dioxide leads to increase of weight and consequently to a decrease in the percentage of nitrogen. Closer investigation shows that a quantity of nitrogen also escapes in the form of ammonia, and that frequently quite considerable quantities of calcium cyanamide are acted on by water with formation of free cyanamide which then polymerises to dicyandiamide.

The action of dicyandiamide on the organisation of the plant is questioned, but the majority consider it injurious in large quantities.[5] H. Kappen examined an old sample of calcium cyanamide, in the aqueous extract of which he only found 115·4 mgm. of N per gram of cyanamide; no further nitrogen in the form of cyanamide could be found, and over 73 per cent. of the nitrogen was present in the form of dicyandiamide.[6] J. P. van Zyl analysed a sample of cyanamide which had been stored for two and a half years in a barn on the naked ground, and found per gram of the material 131·3 mgm. of total nitrogen, 99·5 mgm. of cyanamide nitrogen, and 2·1 mgm. of dicyandiamide nitrogen.[7] Thus, in contrast to the sample previously mentioned, this sample had kept very well. In

[1] *Chem. Ztg.*, 1920, pp. 369, 382; see also *Umschau*, 1920, pp. 488 *et seq.*

[2] *Zeitsch. f. offentl. Gesundheitspflege*, 1917, **47**, part 4, *Zentralb. f. Gewerbe-hygiene*, 1917, pp. 103 *et seq.*; *Zeitsch. f. angew. Chem.*, 1920, i, 1 *et seq.*

[3] *Münch. med. Wochenschr.*, 1919, p. 750.

[4] *Offentl. Gesundheitspflege*, **1919**, **4**, 201.

[5] Hager and Kern, *Zeitsch. f. angew. Chem.*, 1916, i., 221; L. Moller, *Biochem. Zeitsch.*, 1918, p. 85.

[6] *Zeitsch. f. angew. Chem.*, 1918, i., 32.

[7] *Ibid.*, 1918, i., 203.

both cases the remainder of the nitrogen is presumably present as urea.[1]

The dicyandiamide may be determined according to the original method of Caro,[2] or according to the improved methods of H. Kappen,[3] G. Hager and J. Kern,[4] A. Stutzer[5] or F. W. Dafert and R. Miklauz.[6] According to G. Hager and J. Kern, as much as 10 per cent. by weight of water may be added to cyanamide without injury, but with 15 per cent. or more of water there is an increasing conversion into dicyandiamide.

There is a reference in the *Chem. Zentralbl.*, 1920, iv., 123, to work by D. Neyer, R. Gorkou, F. Weiske, P. Mazé, Vila, M. Lemoigne and M. Popp, relating to the transformation products of cyanamide during storage or to fertiliser trials with spoilt cyanamide. There are articles on the investigation of cyanamide containing much dicyandiamide[7] by M. Hene and A. V. Haaren[8] also by P. Liechti and E. Truninger.[9]

It is impossible to consider in detail in this work the use of cyanamide as a fertiliser. Twenty to 100 kg. per $\frac{1}{4}$ hectare are allowed, according to the strength of the cyanamide and the nitrogen requirements of the soil and the crops. Apart from the cyanamide, sufficient phosphoric acid and potash fertilisers must be added, and cyanamide may safely be mixed with potash salts, basic slag, lime and bonemeal before being used, or may be spread together with these materials. It should not be mixed with superphosphate. Cyanamide is spread before sowing, and then worked in with the harrow or plough. In the autumn it is advisable to add 15 to 25 kg. per $\frac{1}{4}$ hectare. As a top dressing, cyanamide can only be used for winter sowing and for meadows before the vegetation revives. As a weed destroyer, 20 to 25 kg. are used per $\frac{1}{4}$ hectare. Certain precautions should always be observed when spreading cyanamide; uncovered portions of the body should be smeared with grease; tight-fitting clothes and good boots are absolutely necessary. One should always spread down the wind; and so forth. Special spreading machines are used for the application of cyanamide on the large scale, such as the one described in German Patent 299,954 of the Elektrizitätswerk Lonza A.G.[10]

[1] F. Muhlert, *loc. cit.*, pp. 245 247.
[2] *Zeitsch. f. angew. Chem.*, 1910, p. 2405.
[3] *Ibid.*, 1918, i., 31.
[4] *Ibid.*, 1916, i., 221, 309; 1917, i, 53.
[5] *Ibid.*, 1916, i., 417.
[6] *Zeitsch. f. landw. Versuchsw. in Osterreich*, 1919, p. 1.
[7] See C. Krauss, *loc. cit.*
[8] *Zeitsch. f. angew. Chem.*, 1918, i., 129.
[9] *Chem. Ztg.*, 1916, pp. 365, 812.
[10] See also *Chem. Ind.*, 1918, Nos. 13–14, and *Technik i. d. Landwirtschaft*, 1920, p. 697.

With regard to the fertilising value we may refer more particularly to numerous communications, experiments and articles by Stutzer, Immendorff, Gerlach, Wagner, Tacke and others, which are summarised in the technical treatise by E. Linter and A. Münzinger, "Kalkstickstoff als Düngemittel"[1] ("Cyanamide as a Fertiliser"). Lipschütz has also published a summary on his experiments with cyanamide (Vienna and Leipzig, 1917). A series of important articles is contained in the propaganda literature of the former Verkaufsvereinigung für Stickstoffdünger G.m.b.H., of Berlin, and in numerous individual publications [2] which we cannot consider here.

The properties of cyanamide are such that many attempts have been made to improve it. If it could be cheaply converted into an effective, durable and harmless new fertiliser, the problems of dusting, change during storage, and so forth, would certainly be solved in a very radical manner at one stroke.[3] The process of manufacture of ammonia from cyanamide will be dealt with later, but we will here consider certain other methods of transformation. The most important of these is the conversion of cyanamide into urea, which occurs according to the following equation :—

$$CaCN_2 + H_2O + CO_2 = CaCO_3 + CN.NH_2$$
$$CN.NH_2 + H_2O = NH_2.CO.NH_2$$

We have already mentioned that the formation of urea may take place in cyanamide on ageing, and P. Mazé, Vila and M. Lemoigne [4] have shown that a whole series of soil bacteria, more particularly *B. prodigiosus*, *B. coli* and *B. cloacæ*, are able to convert the nitrogen in calcium cyanamide into urea. This latter compound is rapidly converted in a rich soil, and slowly in a sterile and acid soil, into ammonium carbonate. H. Kappen [5] has written at length on the production of urea from cyanamide.

Calcium cyanamide powder is added to cold water, avoiding heating as far as possible (as this leads to the formation of dicyandiamide and ammonia) and carbon dioxide is passed through the liquid until all the lime is precipitated and all the free cyanamide is in solution; the whole is then filtered through a suction filter in the usual manner (see, for example, German Patent 302,495 of the Lonza A.G.). The clear filtrate is, for example, acidified slightly with sulphuric acid and then warmed to about 70° C. in presence of manganese peroxide, stannic acid or similar colloids. Under these

[1] Berlin, 1915; *Chem. Ztg.*, 1915, pp. 30, 773.
[2] *Chem. Ztg.*, 1915, Repert., 219; 1916, Repert., 221, 273; 1917, Repert., 73; 1920, *Chem. Techn. Ubers.*, 81.
[3] *Chem. Ztg.*, 1920, p. 158.
[4] *Compt. rend.*, **169**, p. 921 (1919).
[5] "Die Katalyse des Cyanamids," Inaugural Dissertation, University of Jena, 1913.

conditions the cyanamide reacts smoothly with water, forming urea, which may be obtained in long needles by evaporating the aqueous solution; on treating cyanamide solution with hydrogen sulphide or the sulphides of heavy metals (also antimony sulphide, etc.), it is converted into thiourea, $CS(NH_2)_2$ (see Immendorf and Kappen, German pats. 254,574, 256,524, 256,525, 257,642, 257,643, 257,827, 267,206, 267,207). The behaviour of cyanamide solutions has also been studied by Baumann,[1] Jona,[2] Kappen,[3] Reis,[4] Ulpiani,[5] Löhnis,[6] Krüger,[7] and E. Schmidt.[8]

According to German pats. 267,514, 299,132 and 301,262/3, the A.G. für Stickstoffdünger convert the calcium cyanamide from Knapsack, which contains calcium chloride, into urea, by passing into a calcium cyanamide paste so much carbon dioxide only as suffices to form an insoluble intermediate product—namely, the calcium salt of cyanamide carboxylic acid. The whole mass is then filtered; the filter retains all the residues from the calcium cyanamide sludge, together with the calcium salt of cyanamide carboxylic acid, whilst the filtrate contains dicyandiamide and calcium chloride only. The residue is washed, again suspended in water, and converted into $CaCO_3$ and free cyanamide by further treatment with carbon dioxide; the aqueous solution of free cyanamide is then filtered on a vacuum filter. According to German patent 239,309, Stockholms Superfosfat Fabriks A.B. add powdered calcium cyanamide, at a temperature below 50° C., to an acid which forms an insoluble calcium salt, filter, add chalk, filter once more, and finally obtain a pure solution of urea. According to German pat. 285,259, of the Österreichische Verein für Chemische und Metallurgische Produktion in Aussig-a.-E. (now A.G. für Chem. und. Metallurg. Produktion in Karlsbad), the cyanamide solution which is obtained is carefully evaporated to the consistency of a syrup and then treated in the cold with nitric acid of 40° Bé. with very careful cooling. The cyanamide solution should never become alkaline during evaporation and small quantities of free acid, such as nitric or sulphuric acid, are therefore added. The temperature during mixing of the cyanamide and the nitric acid should never exceed + 20° C., as otherwise gases are evolved. If the production of urea nitrate has been properly carried out, the whole solution solidifies to a thick paste. The nitrate is

[1] *Ber.*, **6**, 1371.
[2] *Chem. Zentralbl.*, 1908, i., 516.
[3] *Ibid.*, 1910, i., 1626.
[4] *Ibid.*, 1910, ii., 377.
[5] *Ibid.*, 1910, ii., 1239.
[6] *Ibid.*, 1915, i., 567.
[7] Dissertation.
[8] *Zeitsch. f. angew. Chem.*, 1918, ii., 148.

separated on a suction filter and washed with a concentrated aqueous solution of urea.

The Farbwerke vorm. Meister Lucius and Brüning of Höchst-a.-M., who treat the calcium cyanamide from Knapsack, found that the urea obtained from this product almost always contained a small quantity of ammonium salt, which did not influence its fertilising efficiency, but very considerably lowered its spreading power, as the double salts of urea and ammonia are very hygroscopic. If, however, this urea is mixed with the dry, powdered calcium carbonate residues, which are also produced during manufacture, a fertiliser is obtained which retains its spreading power even during storage, and it is so possible to reduce the high nitrogen percentage of 40 to 46 per cent. to the convenient and usual amount of about 20 per cent., without adding other materials (German patent 304,184). German pats. 311,018 and 311,019 of the same firm deal with details of the manufacture of urea from cyanamide solutions. Catalysts, such as hydrated manganese peroxide, tin dioxide from the double salt, $SnCl_4.NH_4Cl$, lead peroxide, chromium or iron hydroxide, are used in quantities very much less than the weight of cyanamide nitrogen present in solution. G. Zarniko (German pat. 300,632) decomposes calcium cyanamide paste with carbon dioxide in a grinding mill containing balls, lifting cams and lifting pegs, introducing the mixture of calcium cyanamide and water at one end, and removing the decomposed sludge at the other.

The conversion of calcium cyanamide into urea has engaged considerable technical interest for some time. The A.G. für Stickstoffdünger of Knapsack and Höchster Farbwerke operate according to Immendorff and Kappen's process. Urea, which when pure, contains 46·6 per cent. of nitrogen, if used as a fertiliser would signalise a return to the original animal manurial principle. As has already been explained, urea can readily be obtained in a form adapted for spreading, or can be diluted if necessary to contain the normal amount of 20 per cent. of nitrogen. The high contents of nitrogen render it very favourable from the point of view of transport. It is quantitatively absorbed by the plant,[1] so that this concentrated product from calcium cyanamide offers many promising advantages. M. Dolch [2] considers the conversion of cyanamide into urea to offer many possibilities, as "the conversion into ammonium sulphate may now be considered as antiquated." The B.A.S.F., which produces urea in an entirely different manner, is erecting an installation for its manufacture.

[1] H. Kappen, *Chem. Ztg*, 1915, "Repert.," 286.
[2] *Chem. Ztg.*, 1917, p. 376.

In spite of the many advantages which would be entailed by the use of urea fertilisers, Jul. Baumann, of the Österr. Verein, Aussig-a.-E., comes to the conclusion that the production of urea from calcium cyanamide would doubtless offer advantages for certain purposes, but would on the whole play a relatively unimportant part. He continues as follows : "Those who realise the dimensions of the cyanamide industry, and understand the nature of an installation for the manufacture of urea, must admit, even though he were the originator of one of the processes in question, that the conversion of calcium cyanamide into urea offers no radical solution of the problem."[1]

The economic value of the whole process suffers from the fact that it is ultimately necessary to concentrate fairly dilute solutions of urea. The process which is described in German pat. 285,259 replaces this evaporation by a previous concentration of the cyanamide solution, so that a similar quantity of steam is used. Possibly double compounds of urea with salts—such, for example, as urea sodium chloride, $CO(NH_2)_2 + NaCl + H_2O$—could be used in order to isolate it in such form. If, to urea solutions, salts of potash, magnesia, and so on, were added, which combine with considerable quantities of water of crystallisation, evaporation costs would be saved, and urea double salts would be obtained. For the conversion of cyanamide into urea, the sulphuric acid can be replaced by hydrochloric or nitric acid, or a salt may be used which readily yields these acids. In Norwegian pat. 31,431, mixed fertilisers of urea and calcium cyanamide are recommended.

Free cyanamide $N \vdots C.NH_2$,[2] is characterised by a further series of interesting reactions (German Patent 164,724). For example, if it is heated with ammonium chloride to 100° C. in alcoholic solution, the following reaction takes place : —[3]

$$NH_2.C \vdots N + NH_3.HCl = (H_2N)_2C : NH.HCl$$

with production of guanidine hydrochloride. By combination of *methylglycocoll or sarcosine with cyanamide, creatine is obtained*[4] according to the equation :—

$$CN.NH_2 + NH(CH_3).CH_2.COOH = H_2N(NH)C.N(CH_3).CH_2.COOH.$$

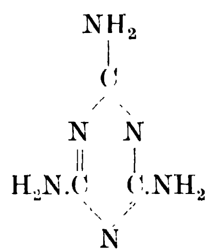
N Caro[5] has described a process of manufacturing indigo from di-alkali cyanamide and phenylglycine, and Farbenfabriken vorm.

[1] *Chem. Ztg.*, 1920, p. 159 ; see also W. O. Herrmann, *Chem. Ztg.*, 1916, p. 915, and Norwegian pat. 30,858.
[2] *Zeitsch. f. angew. Chem.*, 1918, ii., 148.
[3] A. Frank, *Zeitsch. f. angew. Chem.*, 1908, p. 548.
[4] J. Volhard, 1869 ; A. Frank, *Zeitsch. f. angew. Chem.*, 1903, p. 538.
[5] *Zeitsch. f. angew. Chem.*, 1906, p. 839.

Fr. Bayer & Co., of Leverkusen, use cyanamide for the production of cyanacetyl cyanamide (German pat. 151,597). It is probable that none of these reactions are of great technical importance, although guanidine nitrate $CN_3N_5.NO_3H$ has been considered as a possible fertiliser ; it contains an exceptionally high percentage of nitrogen, and is comparatively insoluble in water, and therefore is not readily washed out of the soil, and would probably be a very efficient fertiliser.

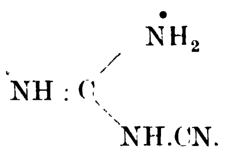
Free cyanamide, certain reactions of which indicate that it may also be considered as carbo-di-imide, $NH = C = NH$, can be obtained from calcium cyanamide in the manner already described (German pat. 252,272). In order to obtain it in a perfectly pure condition rise of temperature must be avoided during its preparation, and it is best to extract the aqueous solution with ether, as at very slightly raised temperatures free cyanamide polymerises, especially in the presence of certain catalysts. Pure free cyanamide forms a colourless crystalline mass, very easily soluble in water, alcohol and ether, melting at 40° C. With ammoniacal silver nitrate solution, $CN.NAg_2$ is precipitated as a yellow salt. Among patents which are concerned with free cyanamide, U.S. pat. 1,093,749 may be mentioned.

The first polymerisation product is dicyandiamide $(CN.NH_2)_2$, which, when heated to 150° C., forms melamin or cyanuramide



and melam, $C_6H_9N_{11}$.

Dicyandiamide,[1] also known as param, or cyanoguanidine,[2] is formed when solutions of free cyanamide are allowed to stand for some time or when its neutral or alkaline solutions are evaporated. It shows a neutral reaction, melts at 205° C., and has the following constitution :—



Some time ago Erlwein was able to show that dicyandiamide is

[1] *Chem. Zentralbl.*, 1920, iv., 725.
[2] F. Muhlert, *loc. cit.*, p. 42.

formed by exhaustive treatment of calcium cyanamide with hot water :—[1]

$$2CaCN_2 + 4H_2O = 2Ca(OH)_2 + (CN.NH_2)_2.$$

It crystallises in white scales from hot solutions. According to German pat. 252,273 and Austrian pat. 45,885/1910 of the Österr. Verein für Chem. und Metallurg. Produktion, in Aussig-a.-E., an aqueous extract of calcium cyanamide is treated with a quantity of ammonia corresponding to half the free cyanamide in solution, and carbon dioxide is passed through the liquid. Dicyandiamide is obtained on evaporating the filtrate. Immendorff und Kappen (German pat. 257,769) [2] heat an alkaline solution of cyanamide in presence of cyanamide compounds of the heavy metals and so obtain dicyandiamide quantitatively.

The Stickstoffwerke. G.m.b.H., of Spandau, who are allied with the Bayrische Stickstoffwerke, mix calcium cyanamide with four times its weight of water in an autoclave. The temperature rises spontaneously to 80° to 90° C. Any ammonia which may be liberated is removed and absorbed. The process is very quickly completed in an autoclave, which is provided with a stirrer. The stirrer is then stopped, the whole allowed to settle, syphoned from the sludge, and the clear, hot solution caused to crystallise. A large quantity of dicyandiamide separates, and is dried in a centrifuge. The mother liquor from these crystals is returned to the process for the extraction of fresh quantities of calcium cyanamide, or is used together with the residual sludge for conversion into ammonia in the autoclave (German Patent 318,136). Alkaline dicyandiamide solutions alone decompose smoothly under pressure, according to the equation :—[3]

$$(CN.NH_2)_2 + 2Ca(OH)_2 + 2H_2O = 4NH_3 + 2CaCO_3.$$

A. Frank [4] proposes the use of dicyandiamide, and more particularly of its derivative, nitrodicyandiamidine, as a "cooling" agent in the manufacture of smokeless powders. According to E. A. Ashcroft (German pat. 252,156) alkali cyanamide or alkali cyanide is obtained by melting dicyandiamide with alkali amide or carbonate, with or without the addition of carbon. This reaction of dicyandiamide appears to be connected with the preparation of cyanide from calcium cyanamide or urea by melting with sodium chloride.[5]

[1] *Zeitsch. f. angew. Chem.*, 1903, p. 520.
[2] See also German pat. 279,133; *Chem. Ztg.*, 1914, "Repert.," 518, 537, and British pat. 25,629/1912.
[3] F. Muhlert, *loc. cit.*, p. 108.
[4] *Zeitsch. f. angew. Chem.*, 1906, p. 839; 1907, p. 1684; *Chem. Ztg.*, 1907, p. 939; British Patent 25,715/1903.
[5] Freudenberg, *Zeitsch. f. angew. Chem.*, 1903, p. 753; Erlwein, *Zeitsch. f. angew. Chem.* p. 535.

Both cyanamide and dicyandiamide can be converted into guanidine and guanylurea or dicyandiamidine $(H_3N_2)CNH.CONH_2$.

Dicyandiamidine is a strongly basic, crystalline substance which may be obtained by the action of dilute acid on its nitrile, dicyandiamide, or on cyanamide itself. It is also produced by melting a guanidine salt with urea [1] and yields a characteristic red copper compound and a yellow nickel compound of the formula $Me(N_4H_5OC_2)_2 + H_2O$, which are used in analytical chemistry.[2]

The Dynamit A.G. vorm. Alfr. Nobel & Co., of Hamburg, convert ammonium nitrate for shell fillings into a form in which it can be cast by adding dicyandiamide, according to German patent 305,567. Ammonium nitrate melts at 152° C., with slight decomposition, and dicyandiamide at 205° C.; but the mixture of 85 parts of ammonium nitrate and 15 parts of dicyandiamide remains liquid at 115° C. According to experiments of J. Baumann, mixtures of dicyandiamide with ammonium nitrate or potassium chlorate in the proportions of 1 to 3 or 1 to 2 may be used as blasting powders :—[3]

$$(CN.NH_2)_2 + 4NH_4NO_3 = 2CO + 6N_2 + 10H_2O$$
$$3(CN.NH_2)_2 + 4KClO_3 = 6CO + 6H_2O + 6N_2 + 4KCl.$$

Calcium cyanamide alone or mixed with other inert salts may be used for face-hardening steel. A well-known face-hardening agent, "ferrodur," is prepared from calcium cyanamide. Its action is probably due to its contents of graphitic carbon, together with "molecular" and cyanogen-carbon.[4] It is possible to replace the potassium ferrocyanide ordinarily used in face-hardening agents by calcium cyanamide.

According to German pats. 116,087 and 116,088 of A. Frank and N. Caro, calcium cyanamide can be converted almost quantitatively into cyanide by heating with carbon and alkali carbonate. On melting with common salt, a 30 per cent. cyanide is obtained.[5] German Patents 265,892 and 267,595 of the Chem. Fabr. von Heyden, of Radebeul, near Dresden, relate to the manufacture of sodium cyanamide or disodium dicyanamide from cyanamide or its polymers and sodium or caustic soda. According to German Patent 149,594 [6] of the Ampére Electrochemical Company, barium cyanamide is converted into acetone by treating it with dilute acetic acid in well-sealed apparatus. Prussic acid is produced, which is absorbed in

[1] *Ber.*, 7, 446.
[2] *Ibid.*, 39, 3356.
[3] *Chem. Ztg.*, 1020, pp. 474, 615.
[4] *Zeitsch. f. angew. Chem.*, 1907, p. 351.
[5] *Chem. Ztg.*, 1903, pp. 520, 533, 543.
[6] *Ibid.*, 1904, p. 364.

caustic alkali, and a solution of barium acetate which yields acetone on dry distillation with re-formation of barium carbonate. The acetone is said to be very pure and cheap. The process has been discussed by A. Neuburger [1] but has never been carried out in practice for any length of time. The B.A.S.F. treats barium cyanide with acetylene at 600° to 800° C. in order to manufacture barium cyanide.[2]

According to German pat. 268,882, O. Ungnade and E. Nolte decompose calcium cyanamide with a mixture of phosphoric and sulphuric acids, in order to obtain a mixed fertiliser containing phosphorus and nitrogen.

Quite new and promising methods are proposed by E. Hene and A. van Haaren. According to German pat. 302,535 they heat monoalkalicyanamide with water above 120° C. Monoalkalicyanamide can be obtained from calcium cyanamide, for example by double decomposition with alkali salts. At temperatures above 120° C. its aqueous solution is smoothly decomposed according to the equation :—

$$2KHCN_2 + 5H_2O = K_2CO_3 + 4NH_3 + CO_2.$$

The decomposition is more rapid and smoother than that of the corresponding calcium compound. The carbon dioxide which is simultaneously formed can be retained with the help of a base or by washing the resulting gases, or in other suitable manner. The reaction velocity increases with the concentration and temperature of the liquor. According to a later German patent, 311,596, the same inventors pass carbon dioxide into an alkali cyanamide solution. The dicyandiamide can be separated from the strong solution during evaporation. The solution of alkali cyanamide can also be treated with nitric acid without appreciable loss if a temperature lower than 60° C. is maintained, and the acid content never exceeds 4 to 8 per cent. On evaporating and crystallising nitrate separates from the urea and other nitrogen products. If the alkali cyanamide solution is neutralised with nitric acid and warmed to 60° to 80° C. for a few hours, then acidified with 4 per cent. of free acid and maintained at 55° C. during 12 hours, during which period the nitric acid which disappears is continuously replaced, both alkali nitrate and dicyandamidine nitrate, which contains very much nitrogen, are obtained. The alkali nitrate is obtained in a pure condition by crystallisation, and valuable mixed fertilisers are obtained by evaporation of the mother liquor to dryness. According to German

[1] *Zeitsch. f. angew. Chem.*, 1905, p. 1810.
[2] *Chem. Ztg.*, 1907, "Repertorium," 97.

pat. 312,392, viscose solutions are stabilised by the addition of calcium cyanamide or its derivatives.

The oldest industrial method of producing more valuable products from calcium cyanamide is to convert it into ammonium salts. Many thousand tons of ammonia have been so obtained in various countries, but this process cannot be considered as an ideal solution of the problem. In principle, it is irrational to convert a finished fertiliser, such as calcium cyanamide, into another fertiliser. Apart from this objection there are a number of disadvantages attached to the manufacture of ammonia from cyanamide, and as M. Dolch expresses it, "The conversion into ammonium sulphate may now be considered as antiquated." [1] The steam requirements of the process are somewhat considerable. The figure obtained on an industrial scale by Jul. Baumann [2] of 331 kg. of steam per 100 kg. of calcium cyanamide is too high, but the amount actually required is sufficiently large appreciably to influence the price of the ammonia which is produced. When a ton of steam could be obtained in Germany at a cost of a very few marks, this was not quite so serious; but this factor is very serious to-day, when the product has to compete with by-product and Haber ammonia, and when it is necessary to produce ammonia at the cheapest possible price for general economic reasons. The higher price for steam, which has increased several fold, is now a serious disadvantage. During the decomposition of calcium cyanamide large quantities of calcium carbonate are obtained as a by-product; no successful use for this has so far been found, and it accumulates to form unsightly heaps during large-scale manufacture. The most obvious method of fixation of the resultant ammonia is to combine it with sulphuric acid to form ammonium sulphate. Considerable quantities of ammonium sulphate were manufactured in this way during and since the War. The shortage of sulphuric acid and its high price have rendered this process relatively unprofitable, but the gypsum ammonium sulphate process can of course be applied to ammonia from cyanamide.

It is improbable that in Germany cyanamide will be converted into ammonium sulphate for very long, but it would be unwise to generalise on this subject. It will be possible for countries in which the sulphuric acid question is not so serious, and in which there is no competition from by-product or Haber ammonia, profitably to convert calcium cyanamide into ammonium sulphate in the future. If the geographical situation is so favourable that cheap water power

[1] *Chem. Ztg.*, 1917, p. 376.
[2] *Ibid.*, 1920, pp. 293-294.

According to U.S. pat. 1,149,653 of W. S. Landis, losses of nitrogen due to the formation of dicyandiamide are avoided by adding salts of alkalies, more particularly sulphates and carbonates. The total yield of nitrogen then amounts to as much as 98 per cent. According to U.S. pat. 1,163,095 of W. S. Landis and the American Cyanamide Company, calcium cyanamide is mixed with alkali hydroxide and treated with superheated steam in autoclaves. A suitable apparatus for carrying out this reaction is claimed by W. S. Landis and the Ammo-Phos Corporation in U.S. pat. 1,183,885. W. S. Landis has repeatedly published exact descriptions of the process of manufacturing ammonia from calcium cyanamide, with the freedom from secrecy which has always distinguished American publications.[1]

The American Cyanamide Company, of which Landis is the technical manager, utilises for the decomposition of calcium cyanamide steel autoclaves of 1·8 m. diameter and 6·4 m. high, which are tested for a maximum working pressure of 20 atmospheres, and which are provided with powerful stirrers on a central shaft. These autoclaves are first charged with 5·5 cu. m. of mother-liquor from the manufacture, or with the corresponding quantity of water. Calcium cyanamide is then gradually added with steady stirring in quantity amounting to one-half to one-third of the weight of liquid. The cyanamide contains about 1 per cent. of carbide, the acetylene from which escapes whilst charging. The charging process takes about one hour; the escaping acetylene is so much diluted that it is no longer explosive. Finally, sodium carbonate and slaked lime are added, which interact with formation of sodium hydroxide and raise the nitrogen yield by preventing the formation of polymers of cyanamide which are difficult to decompose. The autoclave is then closed and steam is introduced for fifteen minutes until the pressure has risen to 3 to 4 atmospheres and the temperature is 133° to 143° C. Under these conditions ammonia is rapidly evolved, and the pressure rises to 12 to 15 atmospheres, although the liberated mixture of steam and ammonia is led away. The reaction then gradually becomes less violent, and is almost complete after one and a half hours. The liquid still contains a quantity of ammonia in solution, and in order to expel this steam is again introduced at a pressure of 6 to 8 atmospheres, and the mixture of ammonia and steam which is now evolved is passed into the condensing plant for a further one and a half hours. A third treatment with steam at 6 to 8 atmospheres yields a further 2 per cent. of ammonia. When the treatment is completed the sludge, consisting of $CaCO_3$, carbon, and so forth, is expelled through a valve in the floor of the autoclave and filtered in

[1] *Met. and Chem. Eng.*, 1916, p. 87; *J. Ind. Eng. Chem.*, 1916, p. 156.

large vacuum filters which separate it into a solid residue and a clear mother-liquor which is returned to the process and used for the decomposition of fresh quantities of calcium cyanamide. The empty autoclave is immediately recharged; 15 autoclaves yield 34 tons of ammonia daily.

W. Grahmann [1] systematically studied the production of ammonia from calcium cyanamide and came to the conclusion that the addition of sodium carbonate or hydroxide accelerates the reaction by forming sodium cyanamide, as it increases the hydroxyl ion concentration. The corresponding potassium compounds do not have quite such a favourable effect, so that the character of the cation appears to have some influence.[2]

In a large munition works in south-west France, an endeavour was made to transform the ammonia oxidation plant into one for the production of ammonium sulphate from cyanamide ammonia. The conclusion was arrived at that it is not always practicable to convert munition works into fertiliser works.[3]

There are lengthy articles on cyanamide and its conversion into ammonium compounds in the *Rev. des Produits Chim.*, **22**, 587 (1919); **23** (1920), 1 and 89.[4]

The impurities in calcium carbide which have already been discussed are re-encountered in calcium cyanamide; more particularly, it contains sulphur compounds, phosphides and silicides. On decomposing the cyanamide with water, these compounds cause the production of gaseous derivatives, such as hydrogen sulphide, hydrogen phosphide, and so forth, which accompany the ammonia [5] and may react with it to form complex compounds. It will be shown below that these impurities in ammonia from cyanamide are particularly objectionable when this is to be oxidised catalytically to nitric acid. It has been found necessary to develop special methods of purification of the crude ammonia gas in this case, as otherwise the oxidation cannot be carried out continuously on a manufacturing scale.

The nitrogen yield during the decomposition of cyanamide varies in well-conducted plants, which work with a good supply of high-pressure steam and where operations are uninterrupted, from 96 to 98 per cent.[6] The sludge from the autoclaves contains not more than 0·1 to 0·3 per cent. of undecomposed nitrogen, but a considerable

[1] *Zeitsch. f. Elektrochemie* **24**, 385 (1918); Lecture at Twenty-fourth General Meeting of the German Bunsen-Gesellsch., of 1918, in Berlin; *Chem. Zentralbl.*, 1919, ii., 405–406.
[2] *Chem. Ztg.*, 1914, "Repertorium," 230, 518.
[3] *Ind. Chimique*, **6**, 43; *Chem. Zentralbl.*, 1919, iv., 536.
[4] Nitricus, *Chem. Zentralbl.*, 1920, ii., 401, 687; iv., 36.
[5] Jul. Baumann, *Chem. Ztg.*, 1920, p. 275.
[6] *Chem. Ztg.*, 1920, p. 275.

amount is present as sulphocyanide in the mother-liquors from the filters. Jul. Baumann has pointed out that it is possible to convert this sulphocyanide into the potassium salt and crystallise it by concentrating the liquid. The salt can readily be obtained in a pure condition by recrystallising from alcohol. It has not so far been produced as a by-product in any cyanamide works. It might, perhaps, be profitable deliberately to increase the sulphur content of the cyanamide in order to obtain larger quantities of this material.[1] The fresh sludge from the filters often contains considerable quantities of sulphocyanide compounds both in soluble and complex forms.

The problem of definitely combining the manufacture of cyanamide ammonia and the ammonia alkali industry has mainly been considered in two publications, namely, German pat. 303,843 of the Bayrische Stickstoffwerke A.G. and N. Caro, and in a publication by Jul. Baumann in the *Chem. Ztg.*, 1920, p. 158. Baumann himself states that he had worked out details of such a process in December, 1911. The principle underlying both processes is the avoidance of the production of calcium chloride solution as a by-product in the manufacture of alkali, and the combination of ammonia with cheap chlorine instead of the dearer sulphuric or nitric acid. The method proposed in German patent 303,843 is as follows: The quick-lime obtained by the calcination of limestone is converted in the usual manner into calcium cyanamide, which is in turn converted into ammonia gas or ammonia liquor. Sodium bicarbonate and ammonium chloride solution are manufactured from sodium chloride, the carbon dioxide from the lime-kilns, and ammonia. The sodium bicarbonate is converted into alkali and carbon dioxide by calcination, whilst solid ammonium chloride is obtained by suitable means from the solution.

Jul. Baumann mentions two methods of working the process suggested by him. According to the first method, ammonia is used in the ordinary manner in the ammonia soda process, and the filtrate from the sodium bicarbonate, which contains on the average 170 gm. of NH_4Cl, 86 gm. of NaCl and 56 gm. of $NaHCO_3$ per litre, is boiled. The dissolved ammonium carbonate is thus decomposed and can be recovered. The residual solution contains 135 gm. NH_4Cl and 124 gm. NaCl per litre. By further evaporation the two salts may be quantitatively separated. According to the second process, the liquor from the sodium carbonate, which contains calcium chloride and considerable quantities of sodium chloride, is treated with cyanamide ammonia and carbon dioxide, thus producing pre-

[1] *Chem. Ztg.*, 1920, pp. 275–276.

cipitated calcium carbonate and a pure solution of ammonium chloride and sodium chloride. These salts can be separated by concentration of the liquor as in the first method.

The ammonia soda process is very wasteful of natural raw materials; the whole chlorine of the sodium chloride is lost, 30 per cent. of the sodium chloride is rejected unchanged in the effluent, and a quantity of lime equivalent to the sodium bicarbonate obtained is also rejected. A combination of the cyanamide and ammonia soda industries would therefore be of economic value; it would relieve the alkali works of their effluents, enable the salt to be rationally used, and dispense with sulphuric acid for fixing the ammonia. Instead of calcium chloride effluent, the calcium carbonate sludge of the cyanamide works would be obtained; and if this could be returned to the process, the cycle would be complete. Jul. Baumann [1] publishes an estimate of the result of his proposed process, which appears to be very favourable; he also recommends the manufacture of ammonium bicarbonate from cyanamide ammonia; there are certain difficulties in drying this product (Austrian pat. 72,870; German pat. 313,827). The B.A.S.F. have also considered the manufacture of ammonium chloride by the ammonia soda process and from ammonium bicarbonate. Agriculturalists generally did not at first view the use of ammonium chloride with favour, although they have for long used a chloride in the form of the potassium salt. These views have only changed very recently. Baumann [2] was able to show that ammonium chloride is quite suitable for admixture with superphosphates.

The plant used in America for the decomposition of cyanamide is based on that used by the Frank-Caro group, as was already mentioned in the economic section of this book. The firm of A. Borsig, in Berlin-Tegel, now supplies complete installations for the manufacture of nitrogen, cyanamide, and cyanamide ammonia. Fig. 11 shows an installation for the decomposition of cyanamide of a capacity of 75,000 tons of the latter product per year of 350 days; it was produced in connection with a project of the A.G. für Stickstoffdünger of Knapsack. The cyanamide from Knapsack, which usually contains very little carbide (0·01 to 0·06 per cent.) is transported to several silos from the cyanamide plant by a horizontal screw conveyor, which is shown in the section, *L–M*. From there it is transported to various smaller storage bins by means of a bucket conveyor; these smaller bins supply the screw con-

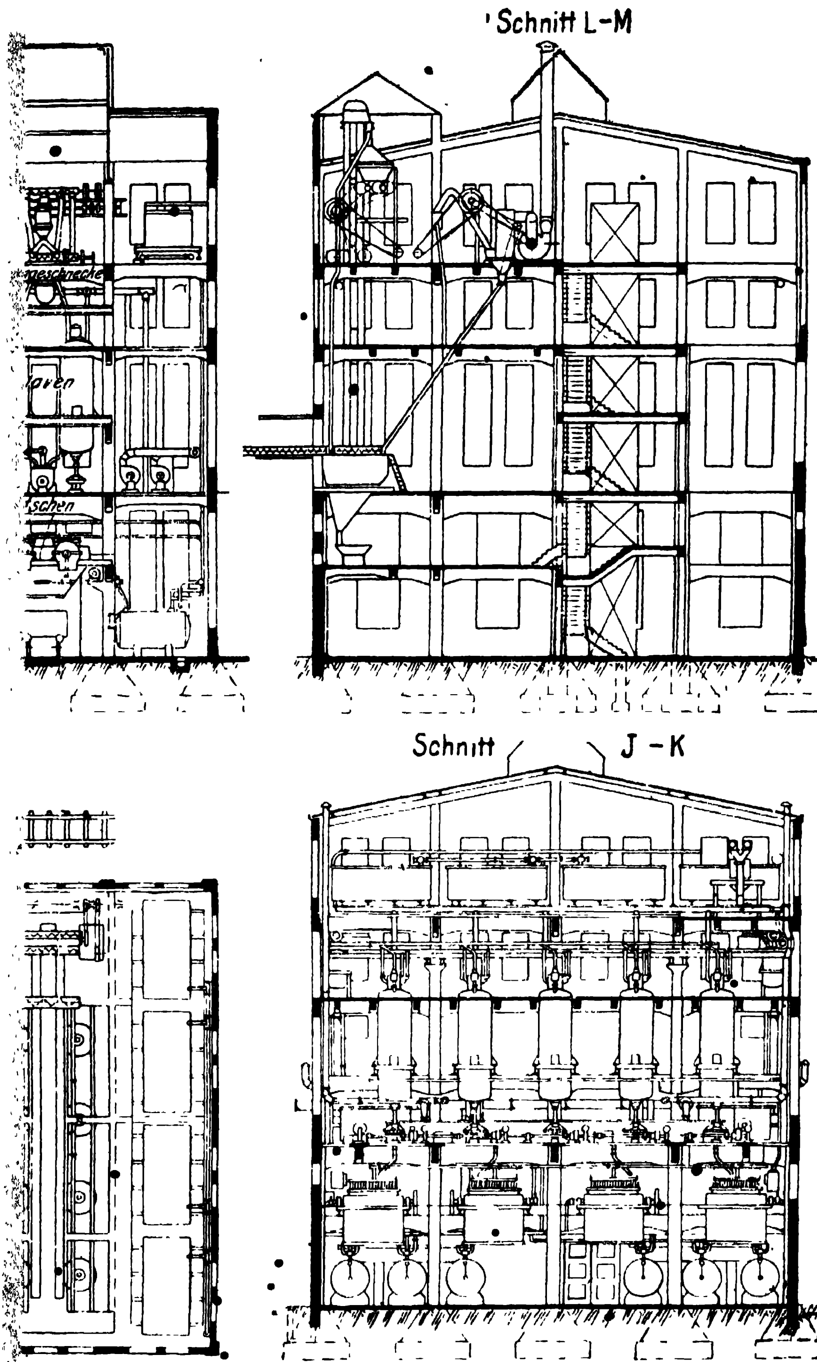
[1] *Loc. cit.*
[2] *Loc. cit.*

veyors which feed the decomposing vessels by way of the automatic weighing machines attached to the same.

In the drawing 40 autoclaves are shown, of which groups of five are supplied by one common screw conveyor (Section J–K). The autoclaves are charged from overhead containers with water or mother-liquor in the manner already described, and cyanamide is then added in certain definite proportions. The cyanamide dust and acetylene gases are removed by suction. The ammoniacal gases which are developed during the actual decomposition are first cooled in four pre-coolers and four final coolers, as is shown in the section. The condensates which are so obtained are led to four distilling plants placed at a lower level, where they are boiled. The ammonia gas which is so obtained passes through the absorption system, where it is finally obtained as concentrated ammoniacal liquor in four cellular coolers. These discharge into four storage tanks from which the aqueous ammonia is transferred to large Intze storage tanks. From these it is either transferred to tank waggons for delivery or otherwise withdrawn as required.

The decomposed autoclave residues are emptied into sludge troughs which discharge on to open vacuum filters. These are provided with vacuum tanks and pumps. The drained sludge residues are discharged directly into trucks by inclining the filters, and are then taken to the dumps.

According to the drawing just described, no special attention is paid to the purification of the ammonia from the autoclaves. Fig. 12 represents an installation of the Berlin-Anhaltische Maschinenbau A.G., which provides for very careful purification of the crude gases. These are delivered to a distilling column, *a*, from which the spent liquor is discharged through the drain-pot, *b*. The vapours of ammonia and steam pass through a water-cooled tubular condenser, *c*, and a similar further cooler, *d*. The condensate from these coolers flows back into the distilling columns, *a*, either directly or through syphon tubes. After passing the second cooler the gases are washed with caustic soda solution in a centrifugal washer, *e*. After being freed from spray in a scrubbing tower, *f*, they pass three wood-charcoal filters, *g*, and are then perfectly pure and almost dry. They are converted into strong ammonia solution in the combined cooling and absorbing apparatus, *h*. The tank, *k*, contains the washing solution; the used wash liquors are freed from ammonia in the distilling column, *i*. The various air vents of the plant are connected with the absorption tower, *j*, where the escaping gases are scrubbed with water in order to avoid



…og = Sludge trough. Schnitt = Elevation. Grundriss = Plan.
…k for sludge removal.

[To face p. 394.

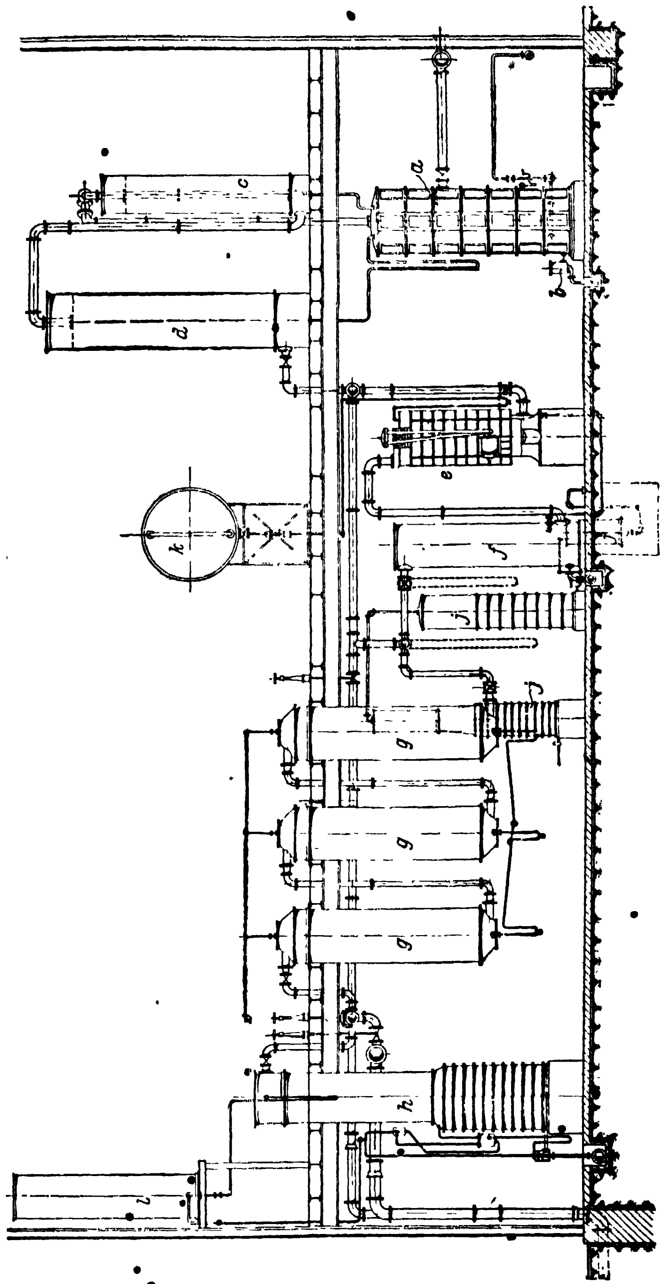


Fig. 12.

loss of ammonia. It is unnecessary to consider here the construction of the individual units of the plant, such as the distilling columns, centrifugal washers, cellular coolers and so forth. They

are of the usual types, which have frequently been described in the literature.[1]

The ammonia gas from the autoclaves may be directly absorbed by sulphuric acid to form ammonium sulphate if it is not thought preferable to use the purified gas for this purpose. Fig. 13 shows a simple installation for this purpose of the Berlin-Anhaltische Maschinenbau A.G. The gases are introduced into the lead saturator, *a*, with a superposed acid trap, *b* ; the acid is introduced through the box, *c*. The sulphate separates as a crystalline paste which is transferred to the pot, *e*, and the draining platform, *d*, by ejectors.

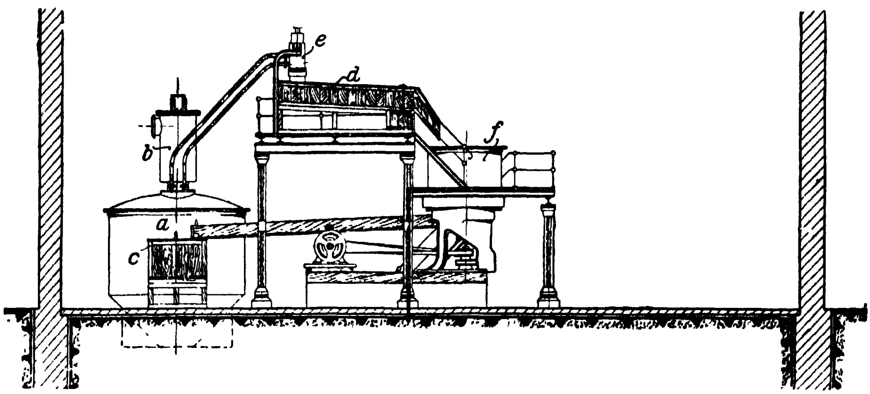


FIG 13.

The liquor passes back from *d* to the saturator, whilst the salt is dried in the centrifuge, *f*.

E. Berl describes the process developed by him, which depends on the following equations :—[2]

$$2CaCN_2 + 2H_2O \quad Ca(OH)_2 + Ca(HCN_2)_2$$

$$Ca(OH)_2 + Ca(HCN_2)_2 + 2NaHSO_4 = 2CaSO_4 + 2H_2O + 2NaHCN_2$$

$$[NaHCN_2 + 3H_2O = NaHCO_3 + 2NH_3 ; \; 2NaHCO_3 = Na_2CO_3 + H_2O + CO_2]$$

$$2NaHCN_2 + 2Ca(OH)_2 + 4H_2O = 2NaOH + 4NH_3 + 2CaCO_3.$$

According to this process the cyanamide is so decomposed, by adding sodium bisulphate, that caustic soda is produced. In contrast to that obtained from cyanamide by the ordinary method, the ammonia so formed is very pure, and may be used without further treatment for oxidation with a platinum contact. During the first years of the War, 60,000 to 70,000 tons of bisulphate were manufactured monthly in Germany by the decomposition of artificial nitrate with sulphuric acid. With the development of concentration

[1] See F. Muhlert, *loc. cit.*, Ullmann's "Encyclopædia," vol. i., etc.
[2] *Chem. Ztg.*, 1920, p. 742.

processes for the dilute nitric acid produced by the oxidation of ammonia the quantity of bisulphate steadily diminished. Whilst Berl's process was of great importance for Germany during the period when sodium bisulphate was available in large quantity, it has unfortunately diminished in importance, since bisulphate is now no longer produced in serious quantities. It may, however, still acquire importance in countries where nitric acid is manufactured from Chile nitrate.

By the ordinary method of decomposing cyanamide a residue is obtained in the autoclave, consisting of a paste which is separated on vacuum filters into a solid residue and a clear liquor which is returned to the process. The rotary filters or suction driers of the firm of R. Wolf A.G., of Magdeburg-Buckau, Werk Ascherslebener Maschinenfabrik, have proved extremely useful for the filtration of the autoclave sludge, as they are able to deal with large quantities of sludge in a relatively short time and filter cloths are not required. Another method is described by Th. Steen in German pat. 315,553 (see also German pats. 314,043, 314,595, 323,297, 324,866).

Many suggestions have, of course, been made to utilise the enormous quantities of autoclave sludge in some way or other. During the War comparatively large quantities were used as a lime fertiliser. The Agricultural Analysis Station at Halle a.d.S. gives the following analyses of sludge from the Piesteritz Works :—[1]

	Per cent.
(a) Water contents in the fresh material from the suction filters	37·4 to 37·95
Water contents in the half-dried material after storage	25·74
Water contents in the stored material .	1

(b) Analysis :—

Total lime . .	32·7 to 48·20 per cent ; average, 38·5 per cent.
$CaCO_3$ . . .	30·23 to 51·60 per cent. ; average, 40·88 per cent.
Total nitrogen (N) .	0·14 to 0·84 per cent. ; average, 0·422 per cent.
Sulphocyanide (CNS)	0·53, 1·24, 1·45 per cent. and traces.

The contents of sulphocyanide vanished during storage by the action of the air. Apart from the very small traces of nitrogen, the fertilising value is entirely due to the calcium carbonate. It should be used in the autumn, and care is necessary on account of the sulphocyanide contents. P. Kessler adds quicklime to the sludge (German pat. 307,244).

[1] *Chem. Ztg.*, 1917, p. 855 ; see also *Chem. Ztg.*, 1914, p. 13.

A market report of August 12th, 1919,[1] gives the following average analysis, and quotes a trade price of 180 marks per 100 kg. at works :—

	Per cent.
$CaCO_3$	35 to 40
N	0·25
$Ca(OH)_2$	15 to 20
C	6
Fe_2O_3	1

When cyanamide is being decomposed at the maximum capacity of the plant a considerable amount of labour and wages are required to dispose of the sludge. Special railway trucks and locomotives must be used for the purpose, and the residues soon accumulate to form obnoxious dumps which take up very much space. These circumstances have led to the practice, in works favourably situated for the purpose, of conveying the autoclave contents, directly without any filtration, into natural cavities, such as old quarries, by means of centrifugal pumps. Natural filtration then takes place through the soil, and the calcium carbonate residue collects in the form of dry masses which gradually fill up the cavities. Any nitrogen still remaining in the liquor in the form of sulphocyanide, complex organic compounds, and so forth, is of course entirely lost by this rough method.

Apart from its commercial use as a fertiliser, the most satisfactory outlet for the lime sludge would be as a raw material for the carbide furnaces. Could this be realised, the lime in the cyanamide process would merely play the part of a carrier which repeatedly returned into the manufacturing cycle.

Jul. Baumann[2] reports that the Vilvorde plant in Belgium, which decomposed cyanamide imported from Odda before the War, had to close because "they were literally choked by their lime sludge." This was, however, by no means the only reason for the ill-success of Vilvorde, which was to a much greater extent due to the difficulties of catalytically oxidising the ammonia which was produced.

In order to re-utilise the sludge in the carbide furnaces, it must first be burnt. If this is done in a rotary furnace, a finely-divided product is obtained. Jul. Baumann[3] reports as follows on the results obtained in a carbide furnace. "The experiments made by a Rhenish cyanamide works gave unsatisfactory results, as the lime which was obtained was for the greater part blown out of the furnace

[1] *Chem. Ztg.*, 1919, p. 540.
[2] *Ibid.*, 1920, p. 562.
[3] *Ibid.*, 1920, p. 275.

by the arc in consequence of its powdery character ; this gave rise to a serious dust nuisance. Nor did the actual process progress in a normal manner. It is also a result of long experience that it is never wise continuously to circulate one of the components in a chemical process as the various impurities always accumulate in such a product and very soon influence the process unfavourably." G. Polysius, of Dessau, adds binding agents, such as potassium or sodium chloride or carbonate, potash mica, schönite, polyhalite or other potash salts to the lime sludge charged into the rotary furnace. The temperature of the furnace is maintained between 900° and 1,200° C. The melting salt cements the lime particles and enables the final product to be obtained in the form of lumps (German pat. 313,595).

At the suggestion of Jul. Baumann,[1] the same firm carried out an experiment with the object of obtaining cement from these residues according to the process of Austrian pat. 78,662 of the Osterr. Verein für Chemische und Metallurg. Produktion in Aussig. The raw materials which were used gave the following analyses after drying at 100° C. :—

Cyanamide Sludge. Per cent.		Clay. Per cent.
3·55	SiO_2	69·40
2·05	$Fe_2O_3 + Al_2O_3$	24·33
43·85	CaO	4·17
Trace	MgO	1·73
0·98	H_2SO_4	—
15·00	Free carbon	—
34·67	Loss on ignition	—

4·71 parts by weight of dried sludge of the above composition were ground with 1 part by weight of clay and ignited at a white heat in an experimental cupola furnace until sintering took place. A perfectly satisfactory material was obtained, the hydraulic modulus of which was 2·09. On analysis the figures obtained were approximately 60 per cent. of CaO, 22·5 per cent. of SiO_2 and 8 per cent. of Al_2O_3, corresponding absolutely to the normal figures for Portland cement. The constancy of volume was perfect, and the tensile strength for the first seven days showed an average of 15 kg. per square centimetre. As the question of a successful further treatment of cyanamide is very closely connected with that of the utilisation of the sludge, this process of cement manufacture, the practicability of which is now proved, may some day become important. According to German pat. 320,442 of the Farbenfabriken vorm. Fr. Bayer & Co., calcium hydroxide sludge is pressed into moulds and the resulting bodies are burnt.

[1] *Chem. Ztg.*, 1920, p. 562.

In the burning and cement manufacturing processes, the carbon contained in the sludge is only of importance in so far as it saves fuel and serves to lighten the mass.[1] This carbon was already identified as graphite by Frank (German pat. 174,846); Frank was able to prove this by oxidising it completely to graphitic acid. A. Remelé and B. Rassow investigated carbon isolated from the Piesteritz cyanamide sludge more closely in order to prove its nature with more certainty.[2] The specific gravity of the material isolated from cyanamide was 2·250, compared with 2·255 in the case of Ceylon graphite. The determination of the electric conductivity, ignition point, and behaviour with potassium chlorate, concentrated nitric acid, molten caustic potash, and so forth, proved beyond any doubt that the carbon obtained according to the equation :—

$$CaC_2 + N_2 = CaCN_2 + C,$$

and which remains unchanged in the sludge produced by the decomposition of calcium cyanamide, actually consists of highly-dispersed carbon of purely graphitic properties. German pats. 112,416 and 174,846 of A. Frank deal with the preparation of graphite from carbide.

In German pat. 297,412, Chem. Fabrik. Griesheim-Elektron emphasise the fact that the graphitic carbon obtained from cyanamide sludge is exceptionally suitable for use as a depolarising agent for dry cells. It is more efficient for this purpose than the best natural graphite.

By homogenisation of cyanamide sludge with oils, for instance, in the Plauson colloid mill,[3] it might be possible to utilise the graphitic contents for lubricating and other purposes.

Finally, in order to illustrate the size of modern cyanamide works, we will give a few figures on the first lay-out of the Piesteritz Works, which have an average output of about 330 tons of carbide or 430 tons of cyanamide daily. There are 8 carbide furnaces which absorb 60,000 kw. of electric energy, 32 trucks of burnt lime, and 22 trucks of coke. The furnace carbide is ground with the help of 4 sets of rolls, 4 rock-breakers, 2 conveyors, 8 mills, and 4 screw conveyors, which carry it to the 720 nitrogenation furnaces. 150,000 cu. m. of pure nitrogen are separated from 210,000 cu. m. of air by means of 6 Linde air compressors and 6 fractionating columns; this nitrogen is converted into about 435 tons of crude cyanamide containing 18 to 20 per cent. of nitrogen. The crude product is converted into approximately 430 tons of marketable

[1] *Chem. Ztg.*, 1920, p. 562.
[2] *Zeitsch. f. angew. Chem.*, 1920, i., 139.
[3] *Chem. Ztg.*, 1920, pp. 553, 565.

product by means of 4 breakers, 4 crushing rolls, 6 grinding mills, 8 elevators, 12 degasifiers, and 6 mixing drums. More than 100,000 cu. m. of cooling water pass through the works daily. Current is supplied by the large power station at Golpa, 25 km. distant, which issued a mortgage in 1920 of 72,000,000 marks, in order to erect a further turbo-generator and the corresponding auxiliary plant. The mortgage was placed abroad, but in terms of German currency.

At Piesteritz 210 tons of cyanamide are decomposed daily in 20 autoclaves and yield 50 tons of ammonia gas, which is converted into 200 tons of ammonium sulphate in 10 saturators, or may be converted into 200 tons of 25 per cent. aqueous ammonia in 6 distilling columns, 18 condensers, and 6 cooled absorbers. The purified gaseous ammonia may, on the other hand, be led to 96 catalytic oxidising units, in which, with the help of a system of condensing towers, it is partially converted into nitric acid, and further into 50 tons of ammonium nitrate and 100 tons of sodium nitrate.

The A.G. für Stickstoffdünger, at Knapsack,[1] has 7 carbide furnaces which consume 5,000 to 6,000 kw. at full load, and supply 200 tons of carbide daily. Details, exact dimensions, and so forth will be found in the literature. The carbide, which is of 77 per cent. purity, is cooled and ground in crushing mortars and in tube mills. The nitrogen is obtained by fractionation of liquid air by Linde's process. The nitrogenation furnaces, which are tunnel furnaces, have already been described. The cyanamide is decomposed in 40 autoclaves, each of about 12 cu. m. capacity, in which 210 tons of cyanamide may be decomposed daily. The gaseous ammonia can be converted into concentrated ammonia solution in the condensation plant which has already been described.

According to Siebner,[2] plant for the decomposition of cyanamide and manufacture of ammonium sulphate existed before the War at Terni, Piano d'Orta in Italy, Paris, Vilvorde in Belgium, Knapsack, Trostberg and Japan. The large German works at Piesteritz and Chorzow,[3] and similar works in France, and particularly in America (American Cyanamide Company at Niagara Falls, which did not decompose cyanamide before the War; the Muscle Shoals Works, etc.), were built during the War.

The French works at Lannamezan contain 20 to 30 carbide furnaces, each of which utilises about 2,000 kw., and 300 Frank-Caro

[1] *Chem. Ztg.*, 1919, p. 810.
[2] *Ibid.*, 1913, p. 1074.
[3] *Chem. Trade Journal*, May 22nd, 1920, p. 665. This contains a description of Chorzow works and details of the agreement between the German Government and the Bayrische Stickstoffwerke.

nitrogenation furnaces. The nitrogen is obtained from liquid air by Claude's process. The Marignac Works contain 6 carbide furnaces, and the carbide is nitrogenated in continuous furnaces of a special type (see above). They produce daily 100 tons of cyanamide containing 22 per cent. of nitrogen and 120 tons containing 15 per cent. of nitrogen. The nitrogen is produced by the Claude process. The Société des Mines de Carmaux owns 8 1-phase carbide furnaces, each of about 2,000 kw. capacity, and 224 Frank-Caro nitrogenation furnaces for an annual production of 46,000 tons of cyanamide.

Very exact descriptions exist of the large American plant at Muscle Shoals [1]; there is a very detailed description, with numerous illustrations and drawings, by Andrew M. Fairly, in *Metall. Eng.*, 1919, p. 8, and by E. E. Wolls and C. F. Mitchell, in the *Electrical World*, 1919, pp. 677, 729, of which it will only be necessary to give a short abstract here.

The power station, which has an average efficiency of 90 per cent., is supplied with 30,000 k.w. from the Government station at Gorgas, in the Alabama Coal Fields, 135 km. distant; it also produces independently 60,000 to 70,000 kw. In the carbide raw material section coal is ground for the lime kilns, the lime is burnt, coke is dried, and the lime crushed. The composition of the limestone is :—

	Per cent.
$CaCO_3$	98·23
$MgCO_3$	0·97
SiO_2	0·49
$Al_2O_3 + Fe_2O_3$	0·30
Moisture and loss	0·07
	100·06

The limestone is burnt in 7 rotary kilns, heated with powdered coal, each of which supplies 100 tons of quick-lime per 24 hours. The mixed charge for the carbide furnaces, when dried and ground, is exactly adjusted by means of two automatic weighing machines, and is then transported to the furnace house by screw conveyors. The carbide house contains 12 furnaces, each 3·66 × 6·7 m. in section and 1·83 m. in height. They are open above and fitted with electrodes in the usual manner. The complete electrode weighs 3,080 kg. The furnaces consume 15,000 to 20,000 amps. at 130 volts. Each furnace is provided with transformers, which convert 8,325 k.w. at 12,200 volts (3-phase current of 60 periods) to 130 volts. The charge is fed into the furnace by hand,

[1] Beautiful illustrations by J. Clyde Marquis, "Made-in-America Fertilisers," in the *Country Gentleman*, March 13th, 1920.

and consists of a mixture of 1,400 kg. of quick-lime and 600 to 620 kg. of dry coke. After 6 hours the furnace is tapped with the help of an auxiliary electrode every 45 minutes. The carbide cooling pans each hold about ½ ton, and are transported to the cooling chamber by an electric locomotive. The average analysis of the crude carbide is as follows :—

	Per cent.
CaC_2	82·30 (301 litres)
C	1·20
CaO	14·72
CaSi	0·06
Ca_3P_2	0·07
CaS	0·13
FeSi	0·72
Remainder	0·80

The grinding shed contains 3 crushers, which crush the carbide to about 32 mm. size. The product is raised by a bucket-conveyor to a silo which feeds 3 grinding mills, which grind it to such a degree that 80 per cent. passes through a 40-mesh sieve and the rest through a 10-mesh sieve. The fine grinding is carried out in 3 tube mills, from which the powdered carbide is charged into 8 steel storage bins ; 85 per cent. of this finely-ground carbide passes through a 200-mesh sieve. The grinding machinery is filled with nitrogen.

Nitrogen is obtained from liquid air by the Claude process. The details of this plant will be further described below. The nitrogen has a purity of 99·9 per cent.

The nitrogenation shed has dimensions of 76 × 169 m., and lies to the south of the carbide grinding shed. There are 16 series, each of 96 nitrogenation furnaces, *i.e.*, 1,536 furnaces in all. These are arranged in 2 groups, each of which comprises 8 rows of a breadth of 30·5 m., there being 96 furnaces in a row. There is a gangway 15 m. broad along the centre of the shed, in which is placed the store for the cardboard containers and tubes. The nitrogenation furnaces themselves are of 1,320 mm. outer diameter and 870 mm. internal diameter ; they are 1,630 mm. high, and thus conform in their dimensions to the usual type. They consist essentially of a steel casing which contains an internal lining 225 mm. thick, consisting of fireproof brick. Into the central space of 870 mm. diameter and cylindrical shape, a cylinder of cardboard is introduced and not a sheet-iron cylinder as is usual in Germany ; this is about 770 mm. in diameter, so that there is about 50 mm. play at the sides. A cardboard sheath is placed in the middle of this cardboard lining and holds the heating electrode, which is 16 mm. in diameter and 2,000 mm. long. The cardboard lining is then filled with 730 kg.

of finely-ground carbide. Each furnace is closed by a double lid, of which the outer is covered with sand. Nitrogen is supplied by a main 200 mm. in diameter which passes between each row of furnaces. Each individual oven is supplied by 2 38-mm. pipes, each of which is provided with a cut-off valve. The first inlet pipe enters at the floor of the furnace whilst the second enters at the side at a height of about 150 mm. The nitrogen is at a pressure of about 75 to 100 mm. water column above atmospheric pressure.

The furnaces are first heated for 20 minutes by single-phase current at 100 volts and 200 to 250 amps., and then for 12 hours at 100 to 150 amps. and 50 volts. The exothermic reaction continues for 28 hours without any further external heat supply; the temperature attains 1,100° C. The furnaces are served by small locomotives driven by benzole which traverse the nitrogen shed on a small gauge track. The crude cyanamide has the following composition :—

	Per cent.
$CaCN_2$	63
CaC_2	2
CaO	13
CaS	1
C	11
SiO_2	3
MgO	2
$Fe_2O_3 + Al_2O_3$	2
Various	3

The cyanamide is first transferred from the nitrogenation shed to the cooling shed, which is 116·6 m. long and 15·2 m. wide, and is located at the southern end of the former. It is provided with two 20-ton overhead cranes. The cyanamide grinding shed is exactly similar to the carbide grinding shed. The hard, previously crushed blocks of cyanamide are ground to such a point that 95 per cent. passes through a 200-mesh sieve. The grinding mills are filled with nitrogen. The finished, ground cyanamide is conveyed to the cyanamide storage shed at the south of the cyanamide grinding shed and stored in 9 large ferroconcrete bins, each of which is 17 × 17 m. in area, and 23·3 m. high.

From there the material is carried to the degasification shed, which covers an area of 15·3 × 24·4 m. It is transported by a screw conveyor and an elevator, which supplies further screw conveyors, which in turn fill the charging funnels of 3 hydro-mixer troughs. These are 0·91 m. wide and 11 m. long; they are open above and contain a central screw which makes 50 r.p.m. and carries stirring arms 408 mm. long. Sufficient water to decompose the carbide is

sprayed into the trucks from above. The crude cyanamide passes through the hydro-mixer at a speed of 15 m. per minute, becomes warm, and falls in a completely dry condition directly into the screw conveyors which carry it into the decomposition shed, which is 91·5 m. further south. The acetylene from the degasification troughs escapes into the air.

The decomposing plant consists of an autoclave shed, a boiler shed, and a filtration plant. The ammonia distillation columns are in the open in front of the decomposing shed. The boiler-house contains four Babcock boilers which are quite independent of the large steam power station and supply high-tension steam at 11 to 12 atmospheres pressure. The decomposing shed covers an area of 24·7 × 77 m., and contains 56 autoclaves with steel walls 38 mm. thick; they are cylindrical, have a diameter of 3·44 m., and a total height of 6·1 m. There is a vertical axial stirrer which revolves 12 times per minute. The degasified cyanamide is transported by a bucket conveyor to iron bins on the uppermost floor of the shed, from where it passes into 14 funnels, from which it is delivered into the automatic weighing machines. A system of 127 mm. screw conveyors is so arranged that it feeds the weighed cyanamide alternately into 16 300-mm. screw conveyors. These latter feed 4 autoclaves each.

The whole arrangement thus completely corresponds to the drawing already referred to of the Börsig plant; in the newest German works the screw conveyor system is replaced by transportable bins which are weighed on stationary weighing machines; these bins are filled with cyanamide and carried to the autoclave which is to be charged by means of an overhead crane.

Before charging the cyanamide into the autoclave, it is charged with 2 per cent. caustic soda solution and 136 kg. of sodium carbonate to a depth of about 2·75 m. The free lime of the cyanamide gradually reacts with the sodium carbonate to form more caustic soda, so that the solution finally contains 3 per cent. of NaOH.; 3·6 tons of cyanamide are then gradually added to this solution by means of the screw conveyor. The acetylene evolved from the 2 per cent. of carbide which the cyanamide contains escapes through a special system of pipes. The autoclave is now closed and exposed to steam pressure. By blowing in steam for 20 minutes at 11 to 12 atmospheres pressure the exothermic reaction

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

is started. The pressure rises rapidly to about 18 atmospheres in consequence of the rapid evolution of ammonia. When this pressure

is attained, the mixture of ammonia and steam is gradually allowed to escape; the pressure only drops after 3 hours. The gas mains are then once more closed, and more steam is introduced, by which means the decomposition is completed in 1·5 hours. The process is most carefully watched in order to ensure that no ammonia escapes through the safety valves or otherwise. The gas from the autoclave contains on an average 25 per cent. of NH_3 and 75 per cent. of steam.

It first enters a ring main, from which it passes through 7 sludge traps into 7 ammonia columns which are in the open. These columns are each 7·6 m. high and about 3 m. in diameter. They contain 16 horizontal, bell-shaped trays, each of which is provided with perforations 100 mm. in diameter, and covers to the same. The crude ammonia gas from the columns passes through two tubular condensers attached to each column, *i.e.*, 14 in all, in which the steam is condensed. The ammonia gas-main, of approximately 711 mm. diameter, divides into two branches of about 500 mm. diameter, of which one conducts about 55 per cent. of the total quantity of gas to the ammonia oxidation plant for conversion into nitric acid; the gas passes on its way into this plant through two holders, each of 550 cu. m. capacity; the other branch leads directly into the ammonium nitrate works, where it serves for the neutralisation of the nitric acid, requiring 45 per cent. of the total ammonia. The ammonia plant has an output of 100 tons of NH_3 per week. The arrangement of the nitric acid and ammonium nitrate plants will be discussed in later chapters.

The decomposed contents of the autoclaves are forced by steam or air pressure through a 228-mm. valve and tube system into the vacuum filter shed. This measures 46 × 47·8 m., and contains 4 sludge troughs with stirrers, each communicating with a series of 5 Oliver rotary filters, of which there are therefore 20 in all. The Oliver filters, which have also proved very serviceable in connection with the cyanide gold extraction process, are described in detail in Ullmann's "Encyclopædia," vol. vi., p. 367. The vacuum is maintained at 507 mm. by 12 vacuum pumps. The filtered solution, which contains 2 per cent. of NaOH, is collected in two storage tanks, from which it is transferred through filters into cooling tanks by 7 centrifugal pumps, each of a capacity of 2·5 cu. m. per minute; these supply the scrubbing liquid to the liquid air plant, and also supply the liquid to the 7 overhead measuring tanks which return it to the autoclaves. The autoclave sludge is not utilised.

In the economic portion of this work we explained that the carbide

and cyanamide industry is closely interconnected with those processes which are concerned with the conversion of carbide into other valuable products, more particularly of organic character. Having discussed the economic side of these questions, we will now give a very short summary of the most important technical developments during recent years.

The first step in the further treatment of calcium carbide for the manufacture of organic compounds is the evolution of acetylene [1]; so many types of plant for this purpose have been described, that we can only refer here to German pats. 297,815, 300,858, 301,513, 301,802, 303,729, 305,776, 309,912, 312,190, 313,241, 313,242, 313,392, 313,966, 317,180, 318,108, 319,412, 323,253, 325,410, 326,245 and Norwegian pat. 30,593. Descriptions of acetylene generating plant have been given by J. H. Vogel, who has also made valuable contributions to the technology of acetylene.[2] The great advantages of acetylene for small-scale illumination first led to the idea that any tinker was qualified to construct acetylene generators. Gradually the dangerous properties of acetylene were realised, which, for example, exclude the use of copper or copper alloys in the construction of the apparatus, and also render it necessary carefully to purify the gas; such precautions are now the subject of laws and regulations.[3] Acetylene is largely used for the autogenous welding of metals.[4]

The manufacture of alcohol from carbide, which is carried out at the Lonza Works, in Switzerland, Burghausen on the Alz, in Scandinavia, and in Canada, depends on the following reactions:—

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2 \text{ (Acetylene.)},$$

In Acid solution with mercury catalyst:— $$C_2H_2 + H_2O = CH_3.COH \text{ Acetaldehyde,}$$

$$CH_3.COH + H_2 = C_2H_5.OH \text{ Ethyl alcohol.}$$

$$CH_3.COH + O = CH_3.COOH \text{ Acetic acid.}$$

Catalytically: $$2CH_3.COOH = CO_2 + H_2O + (CH_3)_2CO. \text{ (Acetone.)}$$

which are all carried out on the industrial scale.[5] According to the manufacturing results at Visp, 2 tons of carbide and 500 cu. m. of hydrogen are required per ton of absolute alcohol.[6] For the production of the carbide and hydrogen, 4,000 kg. of limestone, 2,500 kg. of coal, and 11,000 kw.h. are required. The alcohol is sold to the

[1] *Chem. Ztg.*, 1920, pp. 965 *et seq.*

[2] "Das Acetylen," Leipzig, 1911; also Ullmann's "Encyclopædia," vol. i., pp. 130 *et seq.*

[3] *Chem. Zentralbl.*, 1919, iv., 388; Vogel, pp. 245 *et seq.*

[4] *Ibid.*, 1919, iv., 110.

[5] *Chem. Ztg.*, 1916, p. 979; *Zeitsch. f. angew. Chem.*, 1918, iii., 492; *Zeitsch. Spirit-Ind.*, 1919, p. 16; *Chem. Zentralbl.*, 1919, iv., 281; *Umschau*, 1920, p. 114; *Chem. Zentralbl.*, 1920, iv., 366; *Chem. Ztg.*, 1920, p. 487.

[6] *Chem. Ztg.*, 1920, p. 487.

administration of the Swiss Alcohol Monopoly for 35*s.* 2*d.* (at the pre-war rate of exchange) per hectolitre. Even under the exceptionally favourable power conditions at the Lonza Works it will be difficult to continue the manufacture competitively when normal conditions are restored. In August, 1920, there were already rumours of a considerable reduction in the manufacture. This being the case, the economic soundness of the plan to erect a carbide alcohol installation at Torgau, Province of Saxony, appears to have been questionable. At Torgau it was intended to convert acetylene into ethylene, and then into ethyl sulphuric acid. The project has now been abandoned. According to A. Janke,[1] the following amounts of external thermal energy are required for the production of 1 hectolitre of pure alcohol from the following materials :—

	Cals.
From potatoes	680,000
,, sulphite cellulose liquor .	1,100,000
,, wood	500,000
,, calcium carbide, without water power	4,580,000
,, calcium carbide, with water power	1,400,000

The patents taken out during the last few years comprise : German pats. 297,442, 298,851, 301,247, 305,125, 305,997, 309,103, 309,104, 310,242, 314,210, 315,290, 317,589, 317,703, 318,898, 319,368, 319,476, 321,567, 322,600 ; French pats. 467,515, 479,656, and patent of addition 20,217/1915 ; Norwegian pats. 24,803, 30,251, 30,326, 30,419, 30,490, 30,906, 30,907, 30,948, 30,949, 31,377. Prominent among the patentees are Fr. Bayer & Co., Lonza Works, Konsortium für Elektrochemische Industrie G.m.b.H., of Munich, Chem. Fabrik Griesheim-Elektron and N. Grunstein.

Chem. Fabrik Buckau obtains propylene from acetylene and methane according to German pat. 294,794. Farbwerke vorm. Meister Lucius and Brüning, of Höchst, synthesise the esters of fatty acids, according to German pat. 315,021 by the action of acetylene at a high temperature on an equimolecular mixture of fatty acid and alcohol in presence of the mercury salts of inorganic acids. According to German pats. 300,122 and 324,202, Chem. Fabrik Griesheim-Elektron produces glycoll from ethylene, which is in turn produced from acetylene and hydrogen. In his inaugural dissertation [2] H. P. Kaufmann describes the action of the silent electric discharge on acetylene and G. Kirchhoff [3] describes the preparation of thiophene

[1] *Loc. cit.*
[2] Jena, 1916 ; *Chem. Ztg.*, 1917, "Repertorium," 321.
[3] Dissertation, Zurich, 1916 ; *Chem. Ztg.*, 1917, "Repertorium," 221.

from acetylene. A. Wohl and K. Braünig show that under certain conditions glyoxal can be obtained from acetylene by careful oxidation with ozone.[1] R. Meyer and K. Taeger write on the pyrogenic condensation of acetylene,[2] whilst P. Ruggli deals with derivatives of diaminoacetylene.[3] Remembering that chemical industry already uses considerable quantities of acetylene for the manufacture of chlorine compounds, such as tetrachlorethane, trichlorethylene, and so forth,[4] it is clear that the future possibilities arising out of the production of acetylene, and therefore of carbide, are very considerable, and that the synthesis of organic compounds from carbon and the elements of water is now possible on the largest scale.

Attempts have recently been made, especially in France, to exploit another source of alcohol, namely, its manufacture from the ethylene contained in lighting gas and coke-oven gas ; lighting gas contains 4 to 5 per cent. of ethylene, coke-oven gas more than this, and American natural gas as much as 19·5 to 22·5 per cent. The absorption of ethylene by concentrated sulphuric acid with formation of ethyl sulphuric acid was already observed by Berthelot ; according to investigations by Lebeau and Damiens,[5] this reaction may be so accelerated by the presence of mercury together with vanadic, uranic, tungstic or molybdic acid, that the speed of absorption is comparable to that of carbon dioxide by caustic potash solution. According to E. de Loisy [6] the dilute sulphuric acid obtained on decomposing the ethyl sulphuric acid is used for the manufacture of ammonium sulphate, and the heat contained in the effluent gases is used for concentrating a further portion of the acid.[7]

German pat. 302,929 of Svenska A.B. Gasaccumulator describes the preparation of a particularly suitable porous filling for storing compressed acetylene ; according to German pat. 302,122 of the A.B. Lux, acetylene is dissolved in 95 to 97·5 per cent. alcohol, of which 100 litres dissolve 1,600 litres of acetylene at 1·5 atmosphere pressure (see also German pat. 323,712).

The question of the use of acetylene as a motor fuel is certainly not yet settled, although practical experience in Switzerland so far has not been encouraging.[8] We have already referred in the economic section to the use in Switzerland of acetylene as an admixture with

[1] *Chem. Ztg.*, 1920, p. 157.
[2] *Ber.*, 1920, **53**, 1261.
[3] *Chem. Ztg.*, 1920, *Chem. Techn. Übers.*, 222.
[4] See also K. Arndt, *Chem. Ind.*, 1919, Nos. 22–23.
[5] *Chem. Zentralbl.*, 1913, i., 1229.
[6] *Compt. rend.*, **170**, p. 50 (1920) ; *Chem. Zentralbl.*, 1920, ii., 445, 731.
[7] See also " Das Branntweinmonopol," 1921, No. 12.
[8] See Economic Section and Technical Review of *Berlin Tageblatt*, 1919, p. 78 (No. 12) ; *Chem. Ztg.*, 1920, p. 339 ; *Umschau*, 1920, p. 333 ; *Zeitsch. f. Abfallverw.*, 1920, p. 66 ; *Technik i. d. Landwirtsch*, 1920, pp. 646, 715 ; *Chem. Zentralbl.*, 1920, iv., 232.

lighting gas.[1] Acetylene has also been used for domestic heating. Since the commencement of 1920, acetylene plant has been used in the Palast Hotel at Lausanne, which supplies heating gas for a block of five buildings.[2] During severe winter weather, 800 kg. of carbide are used daily, equal to 400,000 cal., whilst in milder weather 100 to 200 kg. only are required. The *Bulletin de la Société Suisse de l'Acetyléne*[3] emphasises the great economy of acetylene heating compared with heating by coal gas and considers that the use of carbide for this purpose initiates a new development in the art of heating. The gas is produced in a stationary generator provided with all the usual safety devices, which is very simple to work; the gas is mixed with air and burnt in a spiral tube system similar to that used in gas-heated baths. The total hot water for a block of houses could be heated to 70° to 80° C. within twenty minutes.

Acetylene is important for the technical manufacture of carbon. It may either be used as a combustible for the preparation of lamp-black, or it may be directly decomposed with formation of carbon and hydrogen.[4] Methods of utilisation of carbide and acetylene are all the more important as in many quarters the production of carbide is considered as the most suitable method of equalising the load in large electric power stations, particularly in those actuated by water power. (Compare Part I.) The manufacture of carbide really represents the accumulation of electric energy in a stable and permanent form. Each kilogram of the product represents considerable quantities of energy stored in a very small space, and these can be utilised in various ways by evolving the acetylene. For more than one reason, therefore, the development of the cyanamide industry is closely interconnected with the question of the utilisation of carbide and acetylene.

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There are no essential novelties to be reported. Attempts are being made so to modify manufacture as to economise power, to open out other uses for carbide, and to convert calcium cyanamide into more valuable products by modifying its properties or converting it into other bodies.

Carbide Manufacture.—The patent literature is mainly concerned with mechanical charging appliances, electrodes and closed furnaces. German Patents[5] 331,249, 340,368, 328,358, 356,254, 322,889, 326,199,

[1] *Chem. Zentralbl.*, 1919, iv., 847.
[2] *Umschau*, 1920, p. 581.
[3] *Loc. cit.*
[4] Ullmann's "Encyclopædia," vol. vii., pp. 76–77.
[5] These are given not in numerical but in chronological order.

324,802, 331,251, 323,798, 326,220, 328,234 ; U.S. Patent 1,422,135 ; French Patent 529,084.

Removal of Dust from Furnace Gases.—German Patents 267,784, 324,660, 324,443, 324,260, 327,047, 327,046, 326,483, 328,944, 328,826, 328,827, 326,964, 327,047, 327,690, 330,451, 340,635, 343,587, 339,397, 342,793, 346,873, 332,164, 331,511, 331,321, 332,640, 341,456 ; Norwegian Patents 31,695, 32,435 ; U.S. Patent 1,416,769. (Excepting patents dealing with electrostatic methods.) German Patents 325,782, 326,484, 331,381, 331,143, 332,805, 338,058, 338,416, 338,560, 340,825, 339,625, 307,071, 309,132, 340,788, 339,728, 341,073, 343,461, 346,295, 339,728, 339,879, 304,201, 347,599, 349,083, 349,162 ; U.S. Patents 1,409,901, 1,444,092.

Generation and Purification of Acetylene.—German Patents 319,526, 322,165, 323,253, 326,608/9, 326,245, 326,610, 326,935, 330,468, 338,243, 331,431, 331,162, 331,161, 331,164, 331,165, 340,076/7, 339,992, 340,606, 340,675, 340,650, 345,071/2, 344,160, 333,125, 333,266, 345,969, 345,970, 346,638, 354,451, 336,986, 337,694, 337,904, 356,432/3, 332,804 ; Norwegian Patent 32,263 ; British Patent 181,571/1921.

Conversion of Carbide or Acetylene into Acetaldehyde, Alcohol, Acetic Acid, Acetone, etc.—German Patents 305,182, 253,160, 339,493, 339,914, 340,872, 332,202, 350,493, 350,048, 356,175/6, 348,146, 360,443, 369,374 365,432, 369,371, 369,373 368,892, 372,193, 324,202, 373,975, 384,351, 383,258, 384,225, 382,091, 356,507, 345,259, 351,463, 379,596, 329,832, 340,065, 339,492 ; U.S. Patents 1,355,299, 1,410,207, 1,425,500 ; French Patents 496,543, 524,958, 526,129 ; Norwegian Patents 31,822, 33,126, 33,127, 34,741, 35,448 ; British Patent 147,067/1921.

Theoretically important work on the formation of calcium cyanamide has been published by P. Dolch (*Zeitsch. für Elektrochemie*) 1920, **26**, 455), and by V. Ehrlich (*ibid.*, 1922, **28**, 529). According to the former writer, the heat of reaction of the nitrogenation

$$CaC_2 + N_2 = CaCN_2 + C \text{ is } 58{,}700 \text{ cals.}$$

Ehrlich observed that calcium cyanamide commences to decompose at temperatures above 1,100° C., that at 1,200° C. the decomposition is more considerable, and that finally at 1,300° C. pure $CaCN_2$ sublimes without melting. A paper was read by Garaix before the Soc. des Ingenieurs Civils de France on the economics of the calcium cyanamide industry, which he considers to be more favourable than that of the Haber ammonia synthesis. L. Williamson (*Chem. Ind.*, 1923, 226–228) considers that the manufacture of carbide will gradually decline. In *Chimie et Industrie*, iii., p. 438 (1921),

Ch. Pluvinage writes on the yield of the nitrogenation process. Chas. H. Jones writes on the Muscle Shoals plant in *Chemical and Metallurgical Engineering*, **23**, p. 182 (1920). The plant at Dicio-san-Martin in Roumania is described by C. Matignon in *Chimie et Industrie*, **7**, pp. 26–29 (1922).

The most important patents are those of Lidholm, Aktiebolag Nitrogenium (of Stockholm), Bayrische Stickstoffwerke (Berlin), G. A. Blume; A.G. für Stickstoffdünger (in Knapsack), C. Rossi, etc., which are mainly concerned with mechanical improvements in the nitrogenation of calcium carbide.

German Patents 321,618, 325,152, 330,165, 338,275, 326,613, 346,761, 332,477, 329,961, 330,943, 340,366, 300,696, 351,443, 356,997; Austrian Patent 83,694; Norwegian Patents 31,796, 35,192; U.S. Patent 1,401,648/9; British Patents 166,887/1921, 182,134/1922.

Various patents, usually of a more or less mechanical character, are concerned with the liberation of ammonia from calcium cyanamide, or with the addition of alkali.

German Patents 311,959, 321,204, 299,071, 305,082, 331,886, 333,748, 339,627; French Patent 504,325.

Patents for freeing the product from dust have been granted to Schwarzenauer, Savés, l'Azote Français, Stockholms Superfosfat Fabriks, A.B.; A.G. für Stickstoffdünger, Rhenania (Aix-la-Chapelle), Silberrad; Schwartz, Mann, etc. These effect the required results by granulating or by production of granules with the help of water, the addition of shale oil, water glass, algæ, sodium bisulphate, calcium nitrate, silicophosphate, sulphite cellulose liquor, peat litter, pitch, urea nitrate, etc.

German Patents 304,965, 306,237, 348,779, 345,815, 353,049, 353,493, 313,129, 304,282; U.S. Patents 1,399,960, 1,405,202; British Patents 151,989/20, 168,070/21, 174,599/22, 163,137/20; French Patents 522,603, 539,415, 524,099, 540,045, 533,513; Norwegian Patents 32,436, 32,850; Swiss Patents 92,144, 89,958.

The following patents are concerned with the preparation of free cyanamide from calcium cyanamide: German Patents 302,495 (Lonza A.G.), 343,248 (Wargöns A.B.). U.S. Patents 1,380,223 (Lidholm), 1,386,445; Norwegian Patents 33,322, 32,944, 32,945; French Patent 520,633; Swiss Patent 87,964; British Patent 159,866/20.

The following patents are concerned with the production of urea from calcium cyanamide: German Patents 335,663, 337,007, 302,515, 308,441, 346,006, 301,278, 303,855/6, 341,933; British Patents 160,857/21, 179,544/22, 192,703/22, 151,597/8/20, 154,563/20,

154,562/20, 179,934/22, 182,134/22; Norwegian Patents 30,858, 32,135, 32,154/5, 32,401, 31,408, 31,431; U.S. Patents 1,417,277, 1,355,369, 1,360,401/2; Swiss Patents 87,968, 91,154, 91,559, 94,023; Austrian Patent 83,395, which were granted to Chemische Fabrik vorm. Schering, A.G. für Stickstoffdünger (in Knapsack), Meister Luzius u. Brüning, Höchst, the North-Western Cyanamide Company, Soc. des Produits Azotés, Norsk Hydro, Washburn, American Cyanamide Company, etc. They are all concerned with the hydrolysis of primary calcium cyanamide by acids, and the combination of the free cyanamide, which is formed as an intermediate product, with water in presence of catalysts. If phosphoric acid is present in any form, under certain conditions "phosphazote" is produced, containing 11 per cent. P_2O_5 and 11 per cent. N in the form of urea, or under other conditions, Matignon's "superam" is produced containing 41 per cent. N and 11·95 per cent. of water-soluble P_2O_5. The production of guanidine by heating cyanamide with ammonium salts is described in the following patents: German Patent 332,681 and U.S. Patent 1,441,206.

The production of dicyandiamide from calcium cyanamide by hydrolysis with water at 80° in three to four hours is described in German Patent 323,665, and in French Patent 517,711.

The production of cyanides by melting calcium cyanamide with salts or alkalies is described in the patents of Landis, the American Cyanamide Company, Deutsche Gold und Silberscheideanstalt, etc.; German Patents 329,627, 330,194; Norwegian Patent 34,601; U.S. Patent 1,359,257; French Patent 505,400.

The manufacture of alkali, carbonates, potassium nitrate and ammonium salts (in conjunction with the ammonium soda process, etc.) is described in German Patents 332,002, 306,315, 307,011, 299,071, 333,748, 346,244, 353,371, 310,661; Austrian Patent 82,794; Swiss Patent 88,756; U.S. Patent 1,418,618; British Patent 179,544/22, which were granted to von. Hene, v. Haaren, Bambachs Company, Lonza A.G.; Danneel, Kroseberg, Butt, Bayrische Stickstoffwerke A.G., Soc. d'Études Chimiques, etc. These are mainly concerned with the conversion of calcium cyanamide into alkali cyanamide, after which alkali carbonate is formed by boiling, and alkali nitrate by neutralising with nitric acid. See E. Berl and co-workers, *Zeitsch. f. angew. Chem.*, **34**, 1921, p. 517, which is concerned with the interaction of calcium cyanamide with sodium bisulphate to form ammonia and sodium carbonate or hydroxide.

The production of ammonium salts from calcium cyanamide and strong mineral acids is described in German Patents 299,131, 299,141,

300,022, 304,344, 300,141 ; French Patents 522,937, 527,389 ; U.S. Patent 1,413,013.

Mixed fertilisers from calcium cyanamide are described in British Patent 152,779/19 ; Norwegian Patent 35,056.

Analytical references are to be found *inter alia* in *Zeitsch. f. angew. Chem.*, 1920, i., 247–254 ; *Soc. Chem. Ind.*, 1921, **40**, 125, 126, and *J. Soc. Chem. Ind.*, 1922, **14**, 143.

There are articles on the mechanism of the manurial action of calcium cyanamide in *Chem. Zentralbl.*, **1921**, i., 115, 162 ; iii., 386. There is a general article by W. S. Landis in *J. Ind. and Eng. Chem.*, **14**, 143 (1922). A new development consists in the use of calcium cyanamide as a catalyst in the synthesis of ammonia : French Patent 517,327 ; British Patents 140,439/21, 140,550/21, 180,314/21. Organic derivatives are produced by Farbenfabriken vorm. Fr. Bayer & Co. according to British Patent 146,289/21 and German Patent 347,608. According to Pincass (*Chem. Ztg.*, 1923, 253–254), the insoluble nitrogen in calcium cyanamide is present in the form of Si_3N_4.

CHAPTER XIX

Nitride Processes [1]

None of the processes to be discussed in this section have so far been practised on a large scale, but the experiments on the subject and the articles and patents which have been published are of such importance from the standpoint of the technology of nitrogen compounds, that they must be discussed here in their main features, more particularly as the last has probably not been heard of—the Serpek process.[2]

Numerous earlier investigators than Serpek had experimented with aluminium nitride, AlN,[3] without any suggestion of a technical application of this compound. O. Serpek was the first to endeavour to carry out the reaction—

$$Al_4C_3 + Al_2O_3 + 6N = 6AlN + 3CO$$

on a manufacturing scale (German Patents 116,746, 181,991, 181,992, 183,702, 206,588, 216,748, 231,886, 235,213, 325,669). In spite of many improvements introduced by Serpek, it has not been found possible successfully to apply the reaction technically, as the difficulties connected with the plant were found to be too great.

Mehner (German Patent 88,999), Willson (British Patents 21 and 755 of 1892), and Chalmot (U.S. Patent 741,396), had already suggested a general method of reducing a metallic oxide by carbon at the temperature of the electric arc and simultaneously injecting nitrogen in order to form the nitride of the metal. On repeating these processes Serpek found that under the specified conditions no nitride is obtained as such nitrides are none of them stable at the temperature of the electric arc. In this way, and in general at temperatures above 2,000° C., alumina and carbon form a molten mass which contains both carbide and liquid alumina, but no trace of nitrogen.

On the other hand, Serpek found that the absorption of nitrogen by a mixture of alumina and carbon is complete at temperatures at which, in the absence of nitrogen, alumina would not be reduced to the metal, and would not melt as such (German Patent 224,628).

[1] See also W. Moldenhauer, "Die Reaktionen des freien Stickstoffs," Berlin, 1920.
[2] See O. Serpek, "Aluminiumnitrid," in Ullmann's "Encyclopædia," vol. i., pp. 287–295; F. Muhlert, "Die Industrie der Ammoniak und Cyanverbindungen," Leipzig, 1915, pp. 109–119; H. Goldschmidt, *Zeitsch. d. Ver. Deutsch. Ing.*, 1919, pp. 877 *et seq.*; K. Arndt, *Chem. Ind.*, 1919, Nos. 22–23; B. Waeser, *Metallbörse*, 1920, p. 1193.
[3] O. Serpek, *loc. cit.*

He was able to show on an experimental scale [1] that in an electrical resistance furnace the formation of nitride commences at 1,600° C., and becomes energetic at 1,700° C. The carbon monoxide which is formed according to the equation—

$$Al_2O_3 + 3C + 2N = 2AlN + 3CO$$

prevents rapid nitrogenation at 1,600° C. By suitable choice of the furnace, so that diffusion of the gaseous products of reaction ($CO + CO_2$) into the incoming nitrogen is rendered impossible, Serpek was able to lower the point at which nitrogenation commences to 1,450° C. Under such conditions nitrogen is absorbed very rapidly at 1,500° C. to 1,550° C. In German Patent 243,839, the B.A.S.F. enumerate a number of additions which lower the temperature of nitrogenation. A small admixture of hydrogen to the nitrogen causes nitrogenation to start at 1,250° C. (French Patents 448,924 and 450,140).

All such catalysts, with the exception of iron, lower the temperature of reaction, but do not increase the reaction velocity. As a rapid reaction velocity is essential on the manufacturing scale, Serpek uses temperatures of about 1,600° C. as an optimum, particularly when treating bauxite containing iron with producer gas.

Many other workers, apart from Serpek, have studied the chemistry and the thermal conditions of the reaction. More particularly, J. W. Richards gives the following equations [2]:—

$$\begin{array}{ccccc} Al_2O_3 + 3C + 2N & = & 2AlN & + & 3CO \\ (-\ 391{,}600 \text{ cal.}) & & +\ (90{,}900 \text{ cal.}) & & (+\ 87{,}480 \text{ cal.}) \\ & = & -\ 213{,}220 \text{ cal.,} & & \end{array}$$

i.e., the reaction is strongly endothermic. Below 1,500° C. it does not take place to any noticeable extent. For the production of 1 ton of aluminium nitride, the actual reaction would require about $\frac{1}{3}$ k.w. years. Naturally in the actual manufacture the consumption of power is considerably greater, being about twice that amount. In German Patent 224,628, which contains the scientific basis of the process, Serpek himself states that the initial temperature for the fixation of nitrogen by the alumina-carbon mixture is 1,100° C., which is evidently too low. According to him, at 1,800° to 1,850° C. nitrogen fixation takes place extremely rapidly with the formation of a nitride containing 30 per cent. of nitrogen. W. Fraenkel [3] found the temperature of initial nitrogenation to be below 1,400° C.; according to him the reaction becomes very rapid at 1,500° C.[4]

[1] Serpek, *loc. cit.*
[2] *Chem. Ztg.*, 1913, p. 1331.
[3] *Zeitsch. f. Elektrochemie*, 1913, p. 362.
[4] *Chem. Ztg.*, 1913, p. 334.

The reason for the large divergence of temperatures found by various workers is due to the use of carbon of various qualities. P. Askenasy wrote on the experiments carried out on this matter by himself and W. Fraenkel.[1] Soot produced from acetylene proved to be especially reactive, and was followed in this respect by wood charcoal and then by graphite, coke being the least reactive form. The alkali content of wood charcoal accelerates the reaction, and the velocity of reaction is astonishingly increased by the deliberate addition of larger amounts of alkali and by the use of ordinary coke. Following on work by F. Fichter,[2] Joh. Wolf [3] studied the conditions for the preparation of aluminium nitride from its elements. On heating rapidly in an electric resistance furnace at a temperature of 1,990° to 2,000° C., he obtained white, almost chemically pure nitride containing 33·7 per cent. of nitrogen, within an hour. The product begins to volatilise at 1,850° C., with dissociation. The nitride which was obtained was always finely crystalline or in definite hexagonal crystals. With rising temperature the size of the crystals increases and they melt at 2,150° to 2,200° C. at 4·3 atmospheres pressure. F. Fichter and G. Oesterheld ascribe the production of the large crystalline aggregates which are often obtained in technical aluminium nitride to the sublimation of the product. In a tungsten vacuum tube furnace at 14 mm. pressure, aluminium nitride commences to sublime at 1,870° C. (± 20° C.) with partial dissociation, and distils completely at 1,890° C. (± 20° C.). The sublimate contains crystalline nitride together with aluminium metal in the colder portions of the tube.[4]

Aluminium nitride is also dealt with in the dissertations of A. Spengel, Basle, 1913, and W. Koblenzer, Munich, 1915.

The process is also described by O. Serpek himself,[5] and by S. A. Tucker, H. L. Read, J. W. Richards and W. O. Hermann.[6] We may also refer to further articles by F. Fichter and A. Spengler,[7] by N. Czako,[8] and by W. Fraenkel.[9] The industrial application of the Serpek process is criticised in detail by C. Matignon [10] and E. Herre.[11 12]

In 1919 the Internationale Nitridgesellschaft, of Zürich, erected

[1] *Chem. Ztg.*, 1915, p. 807.
[2] *Ibid.*, 1913, p. 356; *Zeitsch. f. anorg. Chem.*, 54, 322 (1907)
[3] *Chem. Ztg.*, 1914, p. 103; *Zeitsch. f. anorg. Chem.*, 87, 120 (1914).
[4] *Zeitsch. f. Elektrochemie*, 1915, p. 50.
[5] *Chem. Ztg.*, 1913, pp. 270, 1196, *Zeitsch. f. angew. Chem.*, 1913, iii., 165; *Osterr. Chem. Ztg.*, 1913, p. 104; *Chem. Ztg.*, 1912, p. 50, "Repertorium," 252, 405, 481, 505, 514.
[6] *Chem. Ztg.*, 1912, p. 1144, 1913, pp. 591, 935; 1914, p. 103.
[7] *Ibid.*, 1913, p. 356; 1914, "Repertorium," 63.
[8] *Ibid.*, 1914, p. 443.
[9] *Ibid.*, 1913, pp. 334, 443.
[10] *Ibid.*, 1914, pp. 894, 909.
[11] *Idid.*, 1914, pp. 317, 341.
[12] *Chem. Zentralbl.*, 1920, iv., 620.

an experimental Serpek plant at Niedermorschweiler, near Mülhouse. The company was then absorbed by the Société Générale des Nitrures, which thus acquired the process. The majority of the later patents are therefore in the name of the latter company, or were patented jointly with O. Serpek.

It was at once apparent that the main difficulty in carrying out the process, which is very simple from a chemical standpoint, was connected with the choice of suitable furnace construction. From the commencement, therefore, the patents were mainly concerned with this question, and the fact that the process has not yet succeeded is due to the non-fulfilment of the necessary requirements.

German Patent 236,044 claims the pre-heating of the alumina and reducing agents in a special chamber, and this principle first receives a practical form in German Patent 239,909, in the shape of a furnace consisting of two super-posed drums which meet at an angle. According to the report of the directors of the Société Générale des Nitrures at the General Meeting on June 30th, 1914, experiments with this type of furnace did not give favourable results.[1] The construction of the furnace was simplified later by the

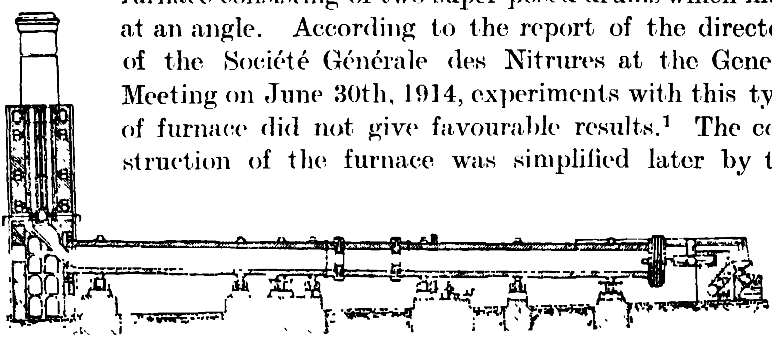

FIG. 14.—Rotary Furnace.

replacement of the upper drum by a tower; but this type of furnace was soon abandoned. German Patent 273,463 describes an electric resistance furnace constructed of wedged-shaped blocks, with internal heating elements. Fig. 14 shows the most modern type of rotary furnace, 60 to 80 m. long and 3 to 4 m. in diameter. The furnace is similarly constructed to a rotary cement kiln, but the heating is carried out electrically and takes place in the centre (German Patents 238,340 and 240,403).

Details on electric heating are described in German Patents 204,403, 244,651, 246,334, 246,931, 246,932 and 248,054 among others. Special resistances were first used, but later the simplest possible form of heating was used, depending on the resistance of the mixture of bauxite and carbon itself. The construction of the electrical part of the apparatus is indicated in Fig. 15. *A* and *B* are massive carbon electrodes which are built up of several units, and are 5 to

[1] Communication from Aluminium Ind. A.G. in Neuhausen, *Chem. Ztg.*, 1914, p. 1266.

8 m. apart, according to the available voltage. The mixture of alumina and carbon fills the intermediate space and acts as a resistance which attains the necessary reaction temperature through the passage of the current. The inclination of the furnace is about 1½ per cent., and its rate of revolution is so arranged that the reaction mass requires about one hour to pass through the electrically-heated portion. Behind the reaction zone the nitride is cooled by the nitrogen passing in the opposite direction, and can be removed from the furnace in a fairly cool condition. The nitrogen is simultaneously pre-heated, so that it enters the reaction zone at a high temperature. The gas leaving this zone contains 60 to 70 per cent. of CO. It naturally has a very high temperature, which it loses in part to the mixture of alumina and coke passing in the opposite direction. The gas is finally burnt in order further to pre-heat the charge, and to calcine the crude bauxite in the uppermost part of the furnace.

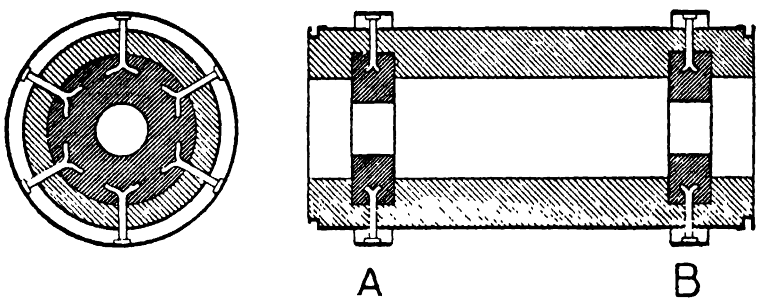

FIG. 15.

Furnaces are built for a current of 2,000 to 8,000 kw. at 200 to 250 volts. In order to maintain the conductivity of the mass in the reaction zone, 30 per cent. more coke or coal must be added than corresponds to the actual reacting proportions. The nitride is itself a bad conductor, even at high temperatures. The excess of carbon, which is not used for reduction of the aluminium oxide, is removed from the nitride leaving the reaction zone by injection of air, thus forming a mixture of nitrogen and carbon dioxide, which is used for the nitrogenation.

The furnace lining in the hottest part consists of aluminium nitride, which is obtained as a crystalline mass for this purpose in special small electric furnaces, in which it is melted.[1]

Though the details of the furnace are well designed, it has not proved satisfactory during continuous working, as the constructional materials themselves have not proved sufficiently resistant to the high temperatures involved.

[1] O. Serpek, Ullmann's "Encyclopædia," p. 292, Fig. 103.

Attempts were then made to lower the temperature and duration of the reaction by the addition of suitable catalysts (German Patents 231,886, 235,213, 235,669, 236,044; French Patents 450,178, 457,109, 457,650, 457,723). It was finally found that by using nitrogen containing hydrogen (French Patents 448,924 and 450,140), alumina containing iron oxide could be nitrogenated at 1,250° C., and it is stated in U.S. Patent 1,078,313 that in a mixture of 30 parts of hydrogen and 70 parts of nitrogen, aluminium nitride is formed at 1,400° to 1,450° C. This modified method has not, however, been utilised on a large scale.

Attempts were made to find a furnace of more durable construction, but these were not successful. The principle followed in these attempts was to obtain an atmosphere of nitrogen by blowing air and pulverised coal into a reaction chamber heated by the arc or by electrical resistances, and to introduce an exactly regulated mixture of bauxite and carbon which was to absorb the nitrogen and thus be converted into aluminium nitride.

The following patents depend on the above principle: German Patents 266,862 (246,419); French Patents 462,464 (463,390), 465,242, 473,918, 474,233, 474,820; U.S. Patents (1,060,640), 1,143,482, 1,217,842; British Patents 27,030/1913, 101,091/1916.

A nitride containing 27·07 per cent. of nitrogen is said to be obtained within one hour at 1,500° C. from a mixture of 10 parts of alumina (from bauxite), with 2·5 parts of carbon, 1·5 parts of manganese carbonate and iron oxide in an atmosphere consisting of 9 parts of nitrogen and 1 part of hydrogen.

The pure nitride obtained at a low temperature from aluminium and nitrogen is white and amorphous. Wolk [1] obtained an impure grey product from aluminium and ammonia. The nitride from the rotary furnace is small in grain, and if obtained from pure alumina is white and free from carbon. Technical aluminium nitride, obtained at higher temperatures, frequently shows green and blue colours. Its crystals are transparent, hexagonal and optically active. The specific gravity rises with the temperature of production, that of the laboratory product, according to Fichter, being 2·88, and that of the technical product 3·18. At atmospheric pressure the nitride does not melt, but sublimes with partial dissociation; according to Serpek the subliming temperature is 2,300° C., but other workers give a figure of 1,850° to 1,890° C.

Hydrogen, carbon, boron, silicon, phosphorus trichloride, sulphur dioxide and hydrogen sulphide do not act on the nitride even at high temperatures. It is decomposed by chlorine on heating, forming

[1] Dissertation, Nancy, 1910.

aluminium chloride and nitrogen, and sulphur monochloride acts in a similar manner. It is only slightly attacked by bromine vapour. It is gradually decomposed by hydrochloric acid forming aluminium chloride and ammonium chloride, whilst carbon dioxide oxidises it to alumina at 1,200° C.

The only reaction of technical importance is the decomposition by boiling water, according to the following equation :—

$$2AlN + 6H_2O = 2NH_3 + 2Al(OH)_3.$$

According to Serpek's lecture to the Verein Österreichischer Chemiker on February 4th, 1913,[1] this reaction proceeds with sufficient rapidity for practical purposes if it is carried out in an autoclave with stirrer at 2 to 4 atmospheres pressure. The ammonia which is liberated distils practically quantitatively under these conditions. Small quantities of alkali aluminate promote the reaction considerably. The decomposed contents of the autoclave, consisting of the insoluble separated aluminium hydroxide, all the impurities in the original bauxite and the catalysts which have been added to accelerate the reaction, are freed from the main portion of the liquid by decantation and then filtered on vacuum or rotary filters. The alkali contents are removed as far as possible by washing. A small residual quantity of alkali is of no consequence, as in presence of coal or coke it accelerates the nitrogenation. The residue on the filter is mixed with further quantities of coke and re-treated in the furnace, forming fresh nitride and completing the cycle of operations. The main quantity of liquid obtained by decantation is mixed with the filtrate and wash-waters, and used for decomposing further quantities of nitride. When carried out in this manner, the process fulfils an ideal of modern technology, in so far as no worthless by-product is obtained. Alumina is not consumed, apart from unavoidable works losses, and merely acts as a nitrogen carrier.

The position is entirely different if the aluminium hydroxide is not returned into the process, but is otherwise utilised. As is well known, the aluminium industry requires very pure alumina as a raw material, and this is obtained from bauxite by various processes, more particularly by the Bayer process, the fundamental principles of which are described in German Patents 43,977 and 65,604. Serpek ingeniously combines the production of aluminium nitride with the manufacture of pure alumina, thus associating the aluminium and nitrogen fixation industries. The whole future of the process now lies in this association, for as a pure nitrogen fixation process it is

[1] *Chem. Ztg.*, 1913, pp. 270–271.

certainly unable to compete, in view of the rapid development of other nitrogen fixation processes; as a source of supply of pure alumina in the form of a by-product, it may possibly have a future. It is from this latter standpoint alone that the process is still receiving technical attention.

If the decomposition of the nitride is carried out with a view to manufacturing pure alumina, the autoclave is not charged with pure water, but with a solution of sodium aluminate of 20° Bé. The aluminium nitride is boiled with this solution for 2 to $2\frac{1}{2}$ hours at 2 atmospheres pressure. The ammonia which escapes during this operation is very concentrated, and can, of course, be treated by any of the usual processes for the production of ammonium salts, just as has already been described in the decomposition of calcium cyanamide.

After the distillation of the ammonia a concentrated solution of aluminate remains in the autoclave, and contains in solution the alumina which has been formed from the nitride during the reaction. The clear solution is separated from any insoluble impurities by decantation, and is then treated for the production of pure alumina by the Bayer process.

By this method a very pure aluminium oxide is obtained in a relatively simple manner from very impure bauxite, containing considerable quantities of iron and silicon, without the use of large quantities of expensive chemicals. The only real difficulty is the choice of a suitable furnace. Serpek describes his combined process (German Patent 241,339) as the Bayer-Nitride process. Whereas the ordinary Bayer process requires aluminate solutions of about 40° Bé., the Bayer-Nitride process only requires aluminate solutions of 20° Bè.; it works at a considerably lower pressure, the decomposition is more rapid, and dilution of the wash liquors is not only immaterial, but necessary in the combined process. In 1913–14 Serpek [1] estimated the production costs of 1 ton of pure alumina by the two processes as follows, the cost of the bauxite in the one case and of the nitride in the other being ignored :—

	Per ton.
Bayer process	100 marks
Bayer-Nitride process	50 ,,

He estimates that, per kilowatt year, 2 tons of pure alumina and 500 kg. of nitrogen in the form of ammonia are obtained. (Goldschmidt calculates that about 17 k.w.h. are required per kilogram of nitrogen in cyanamide.) The production cost of the ammonia at that time was about 24 pfg. per kilogram.

[1] Ullmann's "Encyclopædia," *loc. cit.*

Whilst improvements of the aluminium nitride process itself, for example the production of nitride from ferro-aluminium at 1,250° C., are described in French Patents 474,322, 474,330, 474,365, 476,121, and British Patents 11,091/1913, 21,366/1913 of the Société Générale des Nitrures, of Paris, French Patents 367,124, 415,252, 454,430, and German Patents 241,339 and 271,674 deal with the production of ammonia and regeneration of pure alumina.

Various other processes similar in character to the Serpek process have been developed, but none of these have attained any serious technical importance.

The B.A.S.F., which had also studied the manufacture of other nitrides (see below), has dealt, since 1909, with the manufacture and treatment of aluminium nitride in German Patents 235,300, 235,765, 235,766, 235,868, 236,395, 237,436 and 243,839. The work of the B.A.S.F. has shown that the nitrogenation can be facilitated by the addition of certain oxides to the mixture of alumina and coal, and that the nitride may be partially purified by mild treatment with acids. By the action of concentrated acids or suitable salt solutions, ammonium salts can be directly obtained:—

$$6AlN + Al_2(SO_4)_3 + 24H_2O = 8Al(OH)_3 + 3(NH_4)_2SO_4.$$

In the manufacture of ammonia and alumina the B.A.S.F. uses certain definite methods of purification. When it appeared to the B.A.S.F. that their other nitrogen fixation interests rendered it desirable, they transferred the whole of their nitride patents, including those for the further treatment to produce ammonia, to the owners of Serpek's patents, the Société Générale des Nitrures, of Paris, and thus avoided useless patent litigation which would otherwise have been inevitable. In return the French company granted licences for the use of the Serpek process to the B.A.S.F. and the I.G.

G. Coutagne has described a process in French Patents 457,992 (addition 18,022), 462,462, 466,986, 472,465, and German Patents 322,285, 324,867, which is similar in principle to the Serpek process, and has also been tried on a large scale.[1] He coats, for example, lumps of carborundum with a thin layer of alumina and passes nitrogen, carbon monoxide and, for example, naphthalene vapour over these at the temperature of the electric resistance furnace. See also German Patent 325,474.

The manufacture of silicon and aluminium nitrides and the production of ammonia from these is described by the Norsk Nitrid

[1] *Chem. Eng.*, **3**, 103 (1913).

A.B. in Norwegian Patents 23,290, 23,312 and 23,472. According to Danish Patent 19,449, ferro-aluminium powder containing 40 per cent. of aluminium is treated with nitrogen at 1,250° C. for three hours, and a product is obtained containing about 20 per cent. of N. If an impure bauxite, containing titanium and silicon oxides and about 60 per cent. of Al_2O_3, is converted into impure ferro-aluminium, and this is treated as above described, a mixture of nitrides is obtained containing 18 to 20 per cent. of N. In German Patent 280,686 and French Patent 458,519, W. Zänker describes a tunnel furnace with trucks containing the reaction mass, which is said to be suitable for nitride manufacture; French Patent 459,093 of the same inventor describes the decomposition of nitrides with formation of ammonia. In German Patent 284,531 and the corresponding French Patent 463,232, G.m.b.H. Gebr. Giúlini, of Ludwigshafen, describes a process for the manufacture of aluminium nitride by external heating of a mixture of alumina and coal in nitrogen with the addition of oxides, hydroxides, or salts of the alkali, alkaline earth or similarly acting metals. Drawings and descriptions of a furnace suitable for the reaction, with regenerative heating, are contained in German Patent 295,573. French Patent 451,405 claims the addition of sodium during nitrogenation. Gebr. Giúlini, who are among the largest German manufacturers of alumina, also propose to convert the aluminium nitride which they obtain into pure alumina and ammonia. The nitrogenation process should be particularly valuable when applied to the less pure qualities of bauxite from Hungary, Dalmatia or Germany, for example from the Vogelsberg.

E. Hermann uses an excess of nitrogen containing methane during nitrogenation, and heats the furnace with gas, for example with natural gas (German Patent 319,046). R. W. Wallace and E. Wassmer claim a process in German Patent 321,617, according to which ammonia is obtained from metallic nitrides by a cycle of processes. German Patent 323,523 claims the production of objects from molten alumina. In connection with the Serpek process we may also refer to British Patents 25,630/1913, 29,430/1909, and French Patents 465,265, 465,679, 465,807 and 474,503 of C. Ellis, I. Margoles, L. C. E. Gautrelet, and the Aluminium Industrie A.G. Neuhausen. According to French Patent 465,807, the latter company states, for example, that nitride formation takes place above 2,000° C. if a sufficient supply of nitrogen is assured.

S. Peacock and the International Agricultural Corporation, of New York, melt finely-powdered silicate rock with coke in a reducing furnace filled with nitrogen at 1,400° to 1,600° C., and obtain nitrides

and carbo-nitrides which are decomposed by steam at 5 atmospheres pressure (U.S. Patents 1,129,505, 1,129,721):—

$$2AlN + 3H_2O = Al_2O_3 + 2NH_3$$
$$Al_2C_3N_6 + 9H_2O = Al_2O_3 + 3CO_2 + 6NH_3.$$

U.S. Patent 1,143,132 of S. Peacock deals with the production of aluminium nitride only. This substance may also be produced according to U.S. Patents 1,188,651 and 1,344,153.

The combination of nitrogen with metals and non-metals, other than aluminium, has also been studied,[1] for example in the general patents of Mehner, Borchers and Beck, Roth and the Comp. Bordelaise des Produits Chimiques (German Patents 88,999, 196,323, 197,293; French Patent 440,217). Special attention has been devoted to the nitrogen compounds of silicon as the raw material is attractively cheap. A. Sinding-Larsen and O. I. Storm use either molten silicon alloys or silicon vapour produced directly from minerals rich in silica, which they treat with nitrogen in the electric furnace (German Patents 217,037, 229,638, 231,090; Swedish Patent 36,205). A. Kolb (German Patent 222,237) nitrogenates calcium silicide at over 1,000° C. The production and decomposition of silicon nitride has been dealt with in detail by the B.A.S.F. (German Patents 234,129, 236,342, 236,892, 237,436, 241,510). In the production in the electric furnace, addition of metallic oxides and other substances accelerates the reaction considerably and increases the absorption of nitrogen. The silicon nitrides are not so readily decomposable as the alkaline earth cyanamides, and in order to liberate all the nitrogen in the form of ammonia they have to be boiled with strongly alkaline solutions or preferably melted with caustic soda at 400° C. in a current of steam.

In his master-patent, German Patent 88,919, Mehner refers to the manufacture of silicon nitrides, which he proposes to use directly as fertilisers. He did not succeed in introducing them agriculturally, as the production cost was very high, and also the evolution of ammonia in the soil took place very slowly.[2] O. Frank also recommends the use of mixtures containing silicon nitride as fertilisers in German Patent 248,697.

G. Tofani combines nitrogen with silicon in the form of ferrosilicon.[3] The manufacture of silicon nitride is also dealt with in U.S. Patents 1,093,813 and 1,123,585, according to which, for example, double nitrides, such as $Al_4N_4.Si_3N_4$, are obtained by melting felspar, phosphorite and coal together at 1,600° to 2,000° C. in a

[1] F. Muhlert, *loc cit.*, pp. 14, 109.
[2] *Zeitsch. f. angew. Chem.*, 1905, p. 1762; 1910, p. 1843.
[3] *Chem. Ztg.*, 1914, "Repertorium," 310.

current of gas rich in nitrogen. According to German Patent 311,767, the Verein Chem. Fabriken, in Mannheim, heats, for example, 10 parts of burnt lime, 10 parts of anhydrous calcium chloride, and 3 parts of 90 per cent. ferro-silicon in dry nitrogen for two hours at 850° C. The whole of the combined nitrogen is then liberated as ammonia by boiling water.

Considerable work has also been carried out on titanium-nitrogen compounds. In 1871 Tessié du Motay (French Patent 92,346) found that titanium nitride evolves ammonia in a stream of hydrogen, simultaneously forming compounds poorer in nitrogen, which are converted into the original nitride by absorption of more nitrogen. The B.A.S.F. endeavoured to convert the so-called titanium cyanonitride, $Ti_{10}C_2N_8$, the compound which is also found in blast furnace slag, into ammonia. Titanium nitrogen compounds are extremely stable. It is necessary to melt them energetically with alkali, or better still with oxidising agents (German Patent 202,563), in order to evolve the nitrogen contents quantitatively in the form of ammonia. If catalysts are also present, nitrogen oxides are formed from the ammonia which is produced (German Patent 203,748). In the case of calcium cyanamide attempts to combine the liberation of nitrogen with its oxidation to nitrogen oxide have so far failed, no catalyst having been found which is sufficiently active in promoting the oxidation of ammonia by atmospheric oxygen at the temperatures at which ammonia is liberated.

A compound which behaves similarly to titanium cyanonitride is the titanium nitride manufactured synthetically by the B.A.S.F. by the action of nitrogen on a mixture of 80 parts of titanic acid, 20 parts of wood charcoal, and 2 parts of sodium sulphate (German Patent 203,750; Norwegian Patent 20,198). Titanium nitride manufactured in this manner readily yields ammonia or its salts on melting with oxidising agents (German Patent 204,204), or on treatment with steam in presence of alkaline reagents (German Patent 204,475), or with acids (German Patent 204,847). See also German Patent 204,563.

Neither the silicon nor the titanium nitrides have found practical application, as their treatment is more complicated and difficult than that of aluminium nitride.[1] According to the description in German Patent 300,898, the Norsk A.S. for Elektrokemisk Industri and the Norsk Industri Hypotekbank, of Christiania, obtain titanium oxides which are suitable for further conversion into nitrides. Detailed work has also been carried out on titanium nitrides by Fr. Faye.[2] E.

[1] Serpek, *Chem. Ztg.*, 1913, p. 1197.
[2] Dissertation, Aix-la-Chapelle, 1916.

Podszus prepares solid bodies, crucibles for melting metals, radiators for incandescent burners, and so forth, from the nitrides of titanium, boron, etc., according to German Patents 282,748, 286,992 and 301,540. According to U.S. Patent 1,088,359, S. Peacock and the Du Pont de Nemours Powder Company obtain titanium cyanonitride from titanium dioxide, charcoal and nitrogen under pressure at 2,000° C., according to the equations :—

$$TiO_2 + 6C = TiC_4 + 2CO.$$
$$TiC_4 + 2N_2 = TiC_2N_4 + 2C.$$

Carbonitriles of entirely different composition, as, for example, $Si_3N_4(C_3N_4)_2$, are described by S. Peacock in French Patent 458,168.

Patents of the B.A.S.F. dealing with the nitrides of molybdenum and tungsten (German Patents 246,554, 250,377, 259,647, 259,648, 259,649, 260,010, 265,294) are partly connected with the subject of the Haber-Bosch high-pressure synthesis of ammonia.

Boron nitride was studied at an early stage.[1] Its preparation from boric acid or borates with carbon in a current of nitrogen at a red heat is described in Basset's British Patent 4,338/1879 and Tucker's German Patent 13,392. According to U.S. Patent 816,928, Lyons and Broadwell electrolyse molten borax with the use of a carbon anode which is surrounded by a graphite tube, through which nitrogen is introduced. The boron nitride produced is said to be readily decomposed by steam at 600° C. according to the equation :—

$$2BN + 3H_2O = B_2O_3 + 2NH_3.$$

A. Stähler and I. Elbert [2] nitrogenate mixtures of boric acid and carbon at 1,500° to 1,700° C. at 70 atmospheres pressure. The final product contains 85 to 87 per cent. of BN. According to French Patent 377,683, additional Patent 17,669/1913 and Patent 456,488, the Comp. Française pour l'Exploitation des Procédés Thomson-Houston heats boric anhydride with alkali cyanide in an electric resistance furnace to about 2,000° C. ; another process of manufacture is described by R. Heyder and the General Electric Company in U.S. Patent 1,077,712. We have already referred to the proposals of E. Podszus for obtaining massive bodies of boron and titanium nitrides, according to German Patents 282,748, 286,992 and 301,540. Boron nitride for this purpose, which must be extremely pure, is manufactured according to German Patent 282,701 of Ehrich and Graetz and E. Podszus, from boric acid, carbon and ammonia at about 1,800° C.

[1] Ullmann's "Encyclopædia," vol. ii. (1915), p. 729.
[2] *Ber.*, 1913, p. 2060 and Dissertation; *Chem. Ztg.*, 1913, "Repertorium," 447, 528.

The actual manufacture of vessels from boron nitride according to the above-mentioned patents is described by W. Schmandt [1]:—

"Anhydrous boric acid, obtained by melting at 1,500° C., and cooled by pouring on to metallic plates, is broken up and ground very finely in an air-tight steel mill. Sugar carbon and paraffin are then added as binding agents, and the whole is once more reground with gentle warming; the mass which is thus obtained is extremely plastic. It is moulded into the form of the desired objects, which are then sintered for two hours at 900° to 1,000° C. under greatly reduced pressure in a furnace. Before removal from the furnace the objects are treated for a short time with ammonia, which produces a thin surface layer of boron nitride which protects them from moisture. The bodies are then removed to the actual nitrogenation furnace, where they are once more heated for 30 to 40 hours to 1,000° C. whilst exposed to the action of ammonia. At the end of this period the whole of the boric acid has been converted into boron nitride and very strong, resonant bodies are left, varying in thickness according to the moulding, and which contain a very small amount of iron only as an impurity. The treatment with ammonia can be shortened by working at 12 atmospheres pressure and at 1,200° C. The formation of nitride is then complete in half the time."

Thin rods of boron nitride have been used as carriers of electric lamp filaments on account of their low heat conductivity. Boiling pots produced from boron nitride have been found exceptionally resistant to molten light metals, such as sodium. Temperatures of 1,800° C. may be maintained in electrically heated tubes of boron nitride. Boron nitride is very resistant, not only to high temperatures, but also to temperature fluctuations, though not to the same degree as quartz. At a white heat, however, steam causes violent decomposition and must not be present.

Pure boron nitride is a white, light, amorphous powder which feels like talc, and which is unchanged in oxygen, hydrogen, hydrogen sulphide and iodine vapour. In contact with a flame it shows a greenish white phosphorescence. On heating with water to 200° C., or on melting with caustic potash, powdered boron nitride yields boric acid and ammonia quite smoothly. On heating boron nitride with the oxides of heavy metals, the latter are reduced with formation of nitrogen oxides, so that the atmospheric nitrogen can be converted smoothly into nitric acid with boron catalysts. The re-activity of boron nitride is greatly increased if produced at as low a temperature as possible. Boron nitride dissociates above 2,000° C.[2] It sublimes at

[1] *Techn. Rundsch. des Berl. Tagebl.*, 1919, No. 39.
[2] *Chem. Ztg.*, 1915, "Repertorium," p. 108; also 1916, pp. 957 *et seq.*

above 2,000° C. in a stream of hydrogen, but in a current of ammonia or nitrogen it is still stable at 3,000° C. The dissociation pressure at 1,220° C. is 9·4 mm.[1]

F. Fichter [2] has worked on beryllium nitride, R. Brandt [3] on calcium nitride, K. Kaiser [4] on zinc nitride, and W. Moldenhauer [5] on iron and chromium nitrides. F. Fichter and Ch. Schölly showed that cerium carbide gives no compound similar to cyanamide and no cyanide with nitrogen at 1,250° C., but that the nitrogen simply replaces the carbon in CeC_2. They conclude that the capacity of forming cyanamide and cyanide under such conditions is determined by the nature of the metal.[6]

In U.S. Patents 1,120,682 and 1,123,763, processes are described for the formation of nitrogen compounds in presence of iron (see also Bucher process under "Cyanide processes," below). According to German Patent 257,188, F. Schreiber passes carbon compounds containing nitrogen, such as pyridine sulphonic acids, over materials containing ferric hydroxide at 150° to 200° C. in order to obtain ammonia, whilst O. Rowlands (British Patent 7,740/1913) introduces wool clippings or similar nitrogenous materials into 5 per cent. caustic soda solution and then electrolyses this with iron electrodes at 100° C. and a current density of 25 amps. per square foot. Ammonia is thus smoothly produced by the simultaneous action of electrolytic hydrogen and the iron contacts. According to Strauss [7] molten iron itself absorbs very small amounts of nitrogen only, not more than 0·04 per cent. by weight. On the other hand, by igniting iron in ammonia at 600° to 800° C., as much as 11·1 per cent. of nitrogen may be introduced corresponding to the compound Fe_4N_2.[8]

Magnesium nitride,[9] Mg_3N_2, may be prepared from nitrogen and magnesium, or magnesia and carbon, in the electric resistance furnace. According to Matignon and Lassieur,[10] metallic magnesium commences to absorb nitrogen at 670° C. P. W. Wallace and E. Wassmer use magnesium nitride for the manufacture of ammonia by decomposing it by steam (French Patent 464,692). F. Fichter and Ch. Schölly [11] found that carbon dioxide acts as an oxidising agent on the nitride according to the following equation:—

$$Mg_3N_2 + 3CO_2 = 3MgO + 3CO + N_2.$$

[1] *Chem. Ztg.*, 1914, p. 358.
[2] *Ibid.*, 1915, p. 500.
[3] *Ibid.*, 1914, "Repertorium," p. 505.
[4] *Zeitsch. f. angew. Chem.*, 1914, p. 481.
[5] *Chem. Ztg.*, 1914, p. 747
[6] *Ibid.*, 1920, *Chem. Techn. Übers*, p. 229.
[7] *Zeitsch. f. angew. Chem.*, **27**, 633.
[8] Ullmann's "Encyclopædia," iv. (1916), p. 337.
[9] *Ibid.*, vii. (1919), p. 682.
[10] *Chem. Ztg.*, 1912, p. 30; *Bull. Soc. Chim.* (4), **11**, 262 (1912).
[11] *Chem. Ztg.*, 1920, *Chem. Techn. Übers*, p. 229.

If carbon monoxide carefully freed from the last traces of the dioxide is passed over magnesium nitride at 1,250° C., the main reaction is as follows :—

$$Mg_3N_2 + 3CO = 3MgO + N_2 + 3C.$$

Magnesium nitride dissociates at 1,500° C. under reduced pressure.

The behaviour of calcium is peculiar and resembles that of lithium. As is well known, metallic calcium and hydrogen readily form the hydride (see German Patent 188,570), which is manufactured as a technical product [1] containing about 10 per cent. of CaO and Ca_3N_2, together with about 90 per cent. of CaH_2. At a dull red heat calcium hydride reduces NO_2 to NH_3. With nitrogen it forms nitride and ammonia ; on the other hand, the nitride forms hydride and ammonia in a current of hydrogen at 600° to 800° C., so that the following equilibria are attained :—

$$Ca_3N_2 + 3H_2 \rightleftarrows 3CaH_2 + N_2 \text{ and}$$
$$Ca_3N_2 + 6H_2 \rightleftarrows 3CaH_2 + 2NH_3.$$

The synthesis of ammonia from its elements can thus be relatively easily effected by way of calcium nitride or calcium hydride (see Haber and van Oordt,[2] Erdmann and van der Smissen,[3] Mayer and Altmayer [4]). S. Reich and O. Serpek [5] also investigated the behaviour of calcium hydride. They found that the action of carbon monoxide produces not only methane and hydrogen, but also considerable quantities of formaldehyde. On reducing the carbonates of the alkali and alkaline earth metals with CaH_2, a certain proportion of formate is formed. The action of nitrogen is said to occur according to the following equation :—

$$3CaH_2 + N_2 = Ca_3N_2 + 3H_2.$$

In his German Patent 181,657, Kaiser proposes to treat barium hydride with nitrogen, so forming barium nitride and liberating hydrogen, whereas calcium hydride yields nitride and ammonia under such conditions. According to French Patent 350,966, magnesium behaves similarly to barium.

A synthesis depending on the use of metallic calcium, which is dear, would of course be entirely uneconomical. Therefore the idea embodied in Kaiser's German Patent Application K. 35,962/1908 [6] constitutes a definite advance ; he proposes to replace the calcium by calcium cyanamide. Thus, for example, pure calcium cyanamide or the commercial product is heated in the absence of moisture and

[1] *Chem. Zentralbl.*, 1906, i., 1481.
[2] *Zeitsch. f. anorg. Chem.*, 1904, p. 341.
[3] Liebig's *Annalen*, **361**, 32.
[4] *Ber.*, 1908, p. 3074 ; Ullmann's "Encyclopædia," iii. (1916), pp. 227, 229.
[5] *Chem. Ztg.*, 1920, *Chem. Techn. Übers*, p. 229.
[6] Keler, *Zeitsch. f. angew. Chem.*, 1909, p. 1445.

oxygen in a stream of nitrogen and hydrogen, the gases being led over the material either alternately or simultaneously. According to Kaiser's patent a regular and permanent current of ammonia gas is thus obtained. Dafert and Miklauz [1] contradict Kaiser's statement, which they consider to be due to an experimental error. On treating the nitrides of the alkaline earth metals with hydrogen, they obtained double compounds of the formula $(M)_3N_2H_4$; in the case of barium only they could not obtain the corresponding substance in a pure state, as it promptly decomposed according to the equation :—

$$Ba_3N_2H_4 + H_2 = 3BaH_2 + N_2.$$

On passing hydrogen over barium nitride, ammonia and the hydride are always formed, and the latter regenerates nitride with further quantities of nitrogen. Dafert and Miklauz propose to base a new process of synthetic ammonia production on these reactions, which are quite similar to those claimed by the Verein Chemischer Fabriken, Mannheim, in German Patent 311,234.

The discrepancy between the statements of Kaiser on the one hand, and Dafert and Miklauz on the other has not yet been explained. If Kaiser's statement, that one can start from calcium cyanamide, and therefore from carbide, is actually true, this would constitute a very considerable advance. Nothing further has been heard of the industrial application of Kaiser's method, although F. Muhlert [2] reported in 1914–15 that a company had been formed in Berlin under the name " Azot " for the exploitation of the process. F. W. Dafert and R. Miklauz have described their method in detail in French Patent 474,994, and the corresponding British Patent 16,597/1914. Calcium hydride may be obtained according to A. Kiesewalter's German Patent 311,987. S. Peacock, in U.S. Patent 1,147,184, claims to produce calcium nitride by heating briquettes of lime and coal to 900° to 1,000° C. in presence of hydrogen and nitrogen. In U.S. Patents 1,134,411, 1,134,412, 1,134,413, and 1,134,414, and French Patent 458,168, the same inventor claims to obtain carbonitriles, such as $Ca_3N_2.C_3N_4$, from lime with a 30 per cent. excess of carbon and nitrogen under reduced pressure at temperatures of 1,400° to 1,600° C. according to the equation :—

$$3CaO + 6C + 3N_2 = Ca_3N_2.C_3N_4 + 3CO.$$

These compounds are volatile and may readily be isolated in solid form by condensation. With water under pressure at 200° C., they are decomposed without difficulty according to the equation :—

$$Ca_3N_2.C_3N_4 + 9H_2O = 3CaCO_3 + 6NH_3.$$

[1] Wiener, *Monatshefte*, 1913, p. 1685.
[2] *Loc. cit.*, pp. 114–115.

E. A. Ashcroft claims to combine nitrogen with sodium in presence of finely-divided carbon at pressures varying from 50 to 200 atmospheres. In this manner he claims to have produced di-sodium cyanide according to the equation :—

$$N_2 + 2C + 4Na = 2Na_2CN.$$

He states that this compound evolves hydrogen in presence of ammonia, and is converted into sodium cyanamide which is decomposed by steam in the well-known manner :—

$$2Na_2CN + 2NH_3 = 2Na_2N_2C + 3H_2$$
$$Na_2N_2C + 3H_2O = Na_2CO_3 + 2NH_3.$$

On melting with sodium ferrocyanide, sodium cyanide is obtained together with metallic iron (U.S. Patent 1,186,367) :—

$$Na_4Fe(CN)_6 + 2Na_2CN = 8NaCN + Fe.$$

In U.S. Patent 1,123,584, S. Peacock claims the use of sulphur as a nitrogen carrier. Sulphur or sulphide ores are roasted in such a manner that the roaster gases contain about 80 per cent. N. and 20 per cent. of oxides of sulphur. These gases are then passed over red-hot coal at about 800° C. :—

$$3SO_2 + 12C + 6N_2 = S_3N_4(C_3N_4)_2 + 6CO$$
$$3SO_2 + 18C + 8N_2 = S_3N_4(C_3N_4)_3 + 9CO.$$

The gaseous reaction products which are so obtained are treated with lime-water under pressure at high temperatures :—

$$S_3C_6N_{12} + 18H_2O = 12NH_3 + 6CO_2 + 3SO_2$$
$$S_3N_{16}C_9 + 24H_2O = 16NH_3 + 9CO_2 + 3SO_2.$$

With acids the corresponding ammonium salts are formed with evolution of SO_2 and CO_2.

H. Goldschmidt [1] criticises the Serpek process as follows : "I obtained my information shortly before the War from Professor Matignon, who had reported on the Serpek process. Professor Matignon spoke favourably of the process in general, but said openly that practical success had not been attained. Héroult and Richards were of the same opinion. The process has been greatly advertised. The shares of the Société Générale des Nitrures, of Paris, were initially dealt with at fabulous prices. At the last International Chemical Congress at New York, in 1913, much misleading information was published by interested parties, so that it appears necessary to state that the process is still in an experimental stage, unless practical results have been obtained quite recently of which something would certainly have been heard."

[1] *Zeitsch. d. Ver. Deutsch. Ing.*, 1919, p. 877.

Supplement, 1921—1924.

These processes no longer play an important part, for the time being, since the Serpek process of manufacturing aluminium nitride came to grief on account of the mechanical difficulties involved. Inventive activity in this direction has consequently decreased considerably.

The preparation and decomposition of aluminium nitride is dealt with by the following patents amongst others: German Patents 324,867, 357,899, 343,793, 327,400; Swiss Patents 92,977, 94,150; U.S. Patent 1,415,446 of G. Coutagne; Soc. Générale des Nitrures; Aluminium Industry A.G., Neuhausen; the Aluminium Corporation of Canada, etc. More general considerations are dealt with by C. Toniolo (*Giorn. de Chim. Ind. App.*, **3**, 303, 360), and heats of formation of aluminium nitride by Fichter and Jenny (*Helv. Chim. Acta*, 1922, **5**, 448). Titanium and magnesium nitrides are dealt with in German Patents 321,617, 347,603, 346,122, 321,617; British Patents 160,454/21, 175,989/22; U.S. Patents 1,408,661, 1,411,087; Norwegian Patent 35,191. There are also important patents of more general scope, namely, German Patents 246,122, 305,612; U.S. Patent 1,379,668; and Austrian Patent 87,199. An article on barium nitride by Meyer and Zappner will be found in *Ber.*, **54**, 560, 1921, and on calcium nitride by Ruff and Hartmann in *Zeitsch anorg. allegem. Chem.*, 1922, **121**, 167.

CHAPTER XX

The Haber-Bosch Synthesis of Ammonia[1]

A CONSIDERABLE proportion of the patent and other literature which has been discussed in the previous chapter on the nitride processes forms a link with the purely synthetic process, which has found its most complete development in the Haber-Bosch process.

The direct synthesis of ammonia from its elements was formerly considered to be impossible. In his "Handbook of Inorganic Chemistry," 1881, vol. ii., p. 79, Graham-Otto states that nitrogen and hydrogen cannot be combined either under pressure, or by heat, or by the action of spongy platinum.[2]

Regnault, Morren, Perrot, Chabrier and Donkin,[3] were only able to effect the combination of these two elements to a very small extent by the action of the electric discharge. It was only in 1862 that Fleck first attempted to facilitate the reaction by the action of catalytically active metals. He passed air over red-hot charcoal, and then led the gas so produced, consisting of nitrogen and carbon monoxide, over heated calcium hydroxide, which was intended to facilitate the production of ammonia with liberation of steam. The first technical process is probably that of P. R. de Lambilly (German Patents 74,274 and 78,573, and British Patent 2200/1903), who states that hydrogen and nitrogen readily combine if suitable contact materials, such as pumice, bone-charcoal or platinum sponge are present, and steam, carbon monoxide and carbon dioxide are also added, in order to render possible the formation of ammonium formate or carbonate. The reaction

$$N + H_3 + CO_2 + H_2O = CO\left\langle\begin{matrix} O \cdot NH_4 \\ OH \end{matrix}\right.$$

is stated to occur at 40° to 60° C., and the corresponding reaction with carbon monoxide

$$N + H_3 + CO + H_2O = H \cdot COO \cdot NH_4$$

at 80° to 130° C. Mackey and Hutcheson (British Patent 13,315/1894) blow hot air through a furnace charged with potassium carbonate and charcoal, and thus approximate to the principle of

[1] W. Moldenhauer, "Die Reaktionen des Freien Stickstoffs" (Berlin, 1920).

[2] F. Muhlert, "Die Industrie der Ammoniak und Cyanverbindungen" (Leipzig, 1910), pp. 119 *et seq.*

[3] Waeser, *Chem. Ztg.*, 1913, No. 110; Neuburger, *Zeitsch. f. angew. Chem.*, 1905, p. 1763.

the cyanide syntheses, such as Mehner's German Patent 92,810, U.S. Patent 607,934, and Swiss Patent 13,884. When electrolysing water containing air with platinum electrodes, Davy observed the formation of ammonia at the negative pole and of nitric acid at the positive pole. Nithack (German Patent 95,532) proposed to utilise this principle in practice by saturating water with air at high pressure, and then electrolysing the same. The nitrogen which was fixed was continuously replenished at the same pressure. This process is stated to have yielded quite satisfactory results on a small scale, but on the large scale enormous current losses were soon caused by increasing decomposition of the water (see also U.S. Patent 791,194, and French Patent 368,585). According to Ch. P. Steinmetz (U.S. Patent 1,062,805), ammonium nitrate and ammonium nitrite are readily obtained from steam and air in the electric arc. F. Hlavati (French Patent 453,207) ionises a mixture of nitrogen and hydrogen, obtained, for example, from producer gas freed from carbon monoxide, by electric discharges, and then passes the resulting mixture over contact substances such as platinised asbestos. The electric pre-treatment can be replaced by the activation of the catalyst by radio-active substances, such as pitch-blende and so forth. The Westdeutschen Thomasphosphat-Werke A.G. (German Patents 157,287 and 179,300) also treat producer gases with the silent electric discharge at 15,000 volts and 2 to 2·5 amps. at 60° to 80° C.; they state that in this way they convert about 20 per cent. of the nitrogen, that is, about 8 per cent. of the gaseous mixture, into ammonia. With a mixture of Dowson gas and nitric oxide containing

12	per cent.	H_2
40	,,	NO
44	,,	CO
4	,,	CO_2

at about 80° C. they obtain a gas containing 12 per cent. of ammonia by volume.

None of the proposals just discussed have been so successful as that of H. Ch. Woltereck [1] (German Patent 146,712). Woltereck found that the heated oxides of iron, chromium, and bismuth possess the property of converting stoechiometric mixtures of nitrogen and hydrogen into ammonia. In the case of iron oxide, the optimum temperature is 300° to 400° C. The oxide is first reduced by the gases and then oxidised. This procedure is repeated indefinitely, and it has been found that the presence of the oxidised compounds assists the activity of the catalyst. For example, a mixture of 26 litres of air and 25·48 litres of lighting gas is passed over the catalyst, having

[1] *Chem. Ztg.*, 1908, p. 189.

previously been passed through almost boiling water and thus been saturated with water-vapour. The catalyst is maintained at a temperature of 300° to 400° C., and consists of granulated crystalline ferrosoferric oxide, which is contained in an iron tube of 2 cm. bore. The most suitable velocity for the gaseous mixture is found to be 310 c.c. per minute. The reaction product is absorbed by sulphuric acid. In two and a half hours 0·408 gm. of NH_3 were obtained, corresponding to a 6·3 per cent. yield, calculated on the hydrogen content of the lighting gas, which was 50 per cent. It is stated that a works was erected in Northern Ireland at a cost of £30,000, in which the Woltereck process was tried on a practical scale, but the manufacture was discontinued. Woltereck has also proposed [1] to gasify peat briquettes in a current of air loaded with steam at a temperature below 550° C. Under such conditions combustion occurs slowly without any appearance of flame. A gas is obtained which yields valuable organic compounds and ammonia. Woltereck maintains that during this process a portion of the atmospheric nitrogen is catalytically converted into ammonia, but Caro quite rightly denies this.[2] It is stated that in practice the process was carried out by passing nitrogen and hydrogen over superheated peat as a catalyst. It is alleged that about 5 tons of ammonium sulphate were obtained from 100 tons of peat. Sixty tons of peat were treated hourly, and it is stated that the production cost of the ammonium sulphate was less than half the market price, but the process was long ago abandoned.

It is impossible to consider here all the processes, whether purely scientific or on a practical scale, which preceded the Haber-Bosch synthesis. I will content myself, therefore, with mentioning the names of Regnault, Perrot, Deville, Berthelot, Hemptinne, Findlay, Young, Briner and Mettler, Baur, Müller and Geisenberger, Johnson, Wright, Baker, Mulders, Loew, Brunnel and Woog, Lipski, Billiter, Dafert and Miklauz, McDermott, Le Chatelier, Matignon, Tessié du Motay, Tellier, and also the summaries which have been prepared by Donath-Frenzel [3] and E. Herre.

In 1884, Ramsay and Young [4] investigated the thermo-chemical conditions for the formation and decomposition of ammonia. These were also studied at a later date by Perman,[5] who emphasised the importance of catalysts.

[1] *Chem. Ztg.*, 1908, pp. 189, 941, 1143; 1909, p. 277.

[2] *Ibid.*, 1909, pp. 350, 413, 483, 541; 1910, p. 1334; 1912, pp. 5, 133, 207, 734, 789.

[3] "Die techn. Ausnutzung des atmosphärischen Stickstoffs" (Leipzig, 1907), pp. 175 *et seq.*

[4] Ullmann's "Encyclopædia," vol. i., 1914, pp. 382 *et seq.*

[5] *Chem. News*, **90**, 13, 182 (1904).

As the result of a large amount of careful work, it was considered at the end of last century to be hopeless to attempt to manufacture ammonia by the direct combination of nitrogen and hydrogen.

It was under these circumstances that F. Haber and his pupils started their work on the synthesis of ammonia. We do not know with certainty what caused F. Haber and G. van Oordt to devote themselves in 1903–4 to the study of the ammonia equilibrium at definite temperatures and pressures; it may have been an enquiry from technical quarters [1] as to whether it would be possible to discover a catalyst which would enable ammonia to be produced profitably from its elements on a large scale, or it may have been a communication of the brothers Margulies [2] in 1903, which directed the attention of Haber to the synthesis of ammonia from the elements; the Margulies brothers worked together with Haber from 1903 to 1907. The results of the work of Haber and van Oordt were published in the *Zeitsch. f. anorg. Chem.*[3]

In the first instance, Haber and van Oordt passed a current of ammonia, dried over quicklime, through a bubble counter, and then into a porcelain tube, which was heated to a high temperature in the electric furnace. The catalyst and the thermo-couple were situated in the hottest portion of the tube. At such temperatures ammonia is almost completely decomposed into its elements and equilibrium is attained. The effluent gases were passed through a Volhard flask containing N/50 or N/100 sulphuric acid, and were then once more carefully dried and passed through a second porcelain tube, which was equipped in exactly the same manner as the first and was contained in the same furnace. The newly formed ammonia was also absorbed by sulphuric acid and the residual gas determined by collection in a gas-holder. If it had been possible to determine the ammonia equilibrium both during formation and during decomposition with sufficient exactitude, the quantity of ammonia formed in the two tubes should have been proportional to the volume of undecomposed gas passing through each. The results did not correspond well with this requirement, but were rather inexact for various reasons. Finely divided iron and nickel were used as catalysts, and it was found that the latter was much less active than the former. Under normal pressure it was found that on passing 15·706 litres of gas, measured under normal conditions, at a temperature interval of 1,000° to 1,020° C., only 0·20 parts of NH_3 remained undecomposed per 1,000, and that 0·26 parts of NH_3 were

[1] Jost, "Dissertation" (Berlin, 1908), p. 17.
[2] *Österr. Chem. Ztg.*, 1918, **21**, 27.
[3] *Zeitsch. f. anorg. Chem.*, **43**, 111; **44**, 341; **47**, 42.

formed per 1,000. Haber concluded from his experiments that at 1,020° C., when ammonia is in equilibrium with its decomposition products, 999·76 mols. per 1,000 are decomposed. The value of the constant $\sqrt{K}$ at 1,020° C. was found to be 2,706 according to the following equation : —[1]

$$\sqrt{K}_{1020^\circ} = \frac{(p_{N_2})^{\frac{1}{2}} \cdot (p_{H_2})^{\frac{3}{2}}}{(p_{NH_3})} = \frac{(0{\cdot}25)^{\frac{1}{2}} \times (0{\cdot}75)^{\frac{3}{2}}}{0{\cdot}12 \times 10^{-3}} = 2706.$$

The ammonia equilibrium over iron was finally determined to be as follows at various temperatures :—

Temperature.	Percentage by Volume.		
	Hydrogen.	Nitrogen.	Ammonia.
27° C.	1·12	0·37	98·510
327° C.	68·46	22·82	8·720
627° C.	74·84	24·95	0·210
927° C.	75·00	25·00	0·024
1,020° C.	75·00	25·00	0·012

It was already known that certain metallic nitrides could be converted by hydrogen into hydrides [2] and ammonia, and that, on the other hand, certain hydrides could be reconverted into nitrides by absorption of nitrogen.[3] Thus it appeared possible to use such metals as highly active carriers by consecutive treatment with nitrogen and hydrogen. Prellinger [4] succeeded in obtaining such results to a very slight extent in the case of manganese. Haber and van Oordt now extended their experiments to this metal and to calcium. They found that the reactions between calcium nitride, obtained from calcium and nitrogen, and hydrogen were represented by the following equations

$$Ca_3N_2 + 3\,H_2 \rightleftarrows 3\,CaH_2 + N_2$$
$$Ca_3N_2 + 6\,H_2 \rightleftarrows 3\,CaH_2 + 2NH_3,$$

and led to an equilibrium at 600° C., and that the equilibrium is complete at 800° C. without any considerable yield of ammonia ; even this small amount of ammonia formation could only be attained by treating calcium nitride with hydrogen as in the above equation, but not by nitrogenating calcium hydride. In the case of manganese,

[1] See Haber, "Thermodynamik technischer Gasreaktionen," 1905.
[2] Moissan, *Compt. rend.*, **127**, 4071 (1898).
[3] Guntz, *Compt. rend.*, **132**, 963 (1901).
[4] *Monatsh. f. Chemie*, **15** 395 (1901).

the conditions were similarly unfavourable, and the results obtained later by O. and R. Margulies and by F. Russ [1] with the nitrides of lithium and magnesium showed equally unfavourable yields.

Haber and van Oordt finally came to the conclusion, as a result of their investigations, that, in order to exploit the synthesis of ammonia technically, it would be necessary to discover a material both the hydride and nitride of which showed considerable dissociation pressures and dissociation velocities at about 300° C.

J. Lipski [2] experimented with cerium nitride and found the maximum dissociation pressure of this compound at 600° to 700° C. to be 34 to 40 cm. of mercury.

The reactions

$$3\,H_2 + CeN = CeH_3 + NH_3 \text{ and}$$
$$N_2 + CeH_3 = CeN + NH_3$$

proceed smoothly between 200° and 300° C. without appreciable occurrence of the secondary reaction

$$3\,H_2 + 2CeN = 2CeH_3 + N_2.$$

A gas was obtained containing over 1 per cent. by volume of NH_3. Moisture and presence of oxygen render both the hydride and the nitride inactive. If these substances are absent, the catalytic action diminishes after some time, but it is restored after allowing the catalyst to stand. It was found to be unimportant whether the starting material was perfectly pure cerium dioxide or only the technical product. The results of Lipski were not confirmed either by Haber, Herre, Dafert and Miklauz, or Billiter.[3]

W. Nernst [4] described a method of calculating chemical equilibria from thermal measurements. According to Thomsen the heat of combination of nitrogen and hydrogen to form ammonia at the atmospheric temperature is 12,000 cals. In the case of the ammonia equilibrium the results obtained by calculation differ widely from the figures of Haber and van Oordt, whilst in numerous other cases the calculated and experimental figures agree excellently ; thus, by calculation, a concentration of $1{\cdot}2 \times 10^{-2}$ per cent. of NH_3 corresponds to an absolute temperature of 893°, whereas Haber and van Oordt find this concentration to occur at 1,020 + 273 = 1,293° absolute. In consequence of the great scientific and technical importance of an accurate determination of the ammonia

[1] Zeitsch. f. Elektrochem., 15, 189 (1909) ; Waeser, Chem. Ztg., 1913, No. 110 et seq.
[2] Zeitsch. f. Elektrochem., 15, 189 (1909) ; Waeser, Chem. Ztg., 1913, Nos. 110 et seq.
[3] Ullmann's "Encyclopædia," vol. i. (1914), p. 391 ; Zeitsch. f. Elektrochem., 19, 54 (1913) ; Monatsh. f. Chemie, 33, 911 (1912) ; Nernst, "Festschrift" (Halle, 1912), p. 86.
[4] Jost, "Dissertation" (Berlin, 1908), p. 19.

equilibrium, W. Nernst and F. Jost decided on a redetermination in 1906–7. The results of their very careful work were published in the *Zeitsch. f. Elektrochem.*, **13,** 521 ; **14,** 373 ; and in the *Zeitsch. f. anorg. Chem.*, **57,** 414. They are also the subject of the "Dissertation" of F. Jost,[1] which may be described as one of the most important landmarks in the history of the development of the direct synthesis of ammonia. It is characteristic of these determinations that they were carried out at high pressures, as, according to the law of mass action, the increase of pressure increases the concentration of ammonia, and also enables equilibrium to be more rapidly attained. E. Maurer [2] is therefore correct in his view that Jost's determinations carried out in Nernst's laboratory really contained all that was necessary as a scientific foundation for the technical synthesis of ammonia. Jost's determinations were fully confirmed by Haber at a later date, but the latter then adopted still higher pressures for working out his practical process. At the conclusion of the work of Jost and Nernst, the effect of a further increase of pressure was quite obvious ; it was, however, generally considered that the relatively low concentration of ammonia which was attained at pressures as high as 74·5 atm. would render the direct synthesis of ammonia practically useless. As a matter of fact, no interest was shown at the time in technical circles in the publication of Jost and Nernst. The splendid results which were embodied in the enormous works at Oppau and Merseburg-Leuna are due to the energetic efforts of the B.A.S.F., which brought the activities of Haber and C. Bosch into association.

Nernst and Jellinek first used the electrical high-pressure furnace [3] devised by the former, which enabled them to work at pressures up to 160 atm., and temperatures of 1,200° C. The results showed that the figure given by Haber for the ammonia equilibrium constant was about four times too high. Meanwhile, Haber and Le Rossignol [4] had improved their methods, and had obtained more accurate and consistent figures and a much lower yield of ammonia than was indicated by the original determinations. F. Jost [5] then carried out a number of exact determinations, after adding various improvements to the original apparatus. By introducing a fine porcelain capillary he ensured the rapid removal of the gaseous mixture from the equilibrium zone. The front portion of the porcelain reaction tube was filled with pure asbestos fibre, so that the possibility of the catalyst being blown into the cold portion of the tube by heavy gas

[1] Berlin, April 15th, 1908.
[2] *Zeitsch. f. anorg. u. allgem. Chem.*, 1919, p. 273.
[3] *Zeitsch. f. Elektrochem.*, 1907, p. 521.
[4] *Ber.*, **40,** 2144.
[5] "Dissertation" (Berlin), 1908.

pressure was absolutely avoided. The mixture of 1 volume of nitrogen with 3 volumes of hydrogen was obtained by allowing nitrogen from a cylinder filled at 100 atm. pressure to enter another cylinder containing hydrogen at 60 atm. pressure until the pressure in the former cylinder was reduced to 80 atm. The nitrogen must be absolutely free from oxygen, and the mixture of nitrogen and hydrogen is therefore passed through a long copper tube about 50 cm. long, containing platinum asbestos at 300° C. The water which is formed is absorbed in a copper tube containing calcium chloride. The pressure was measured by a manometer, which was calibrated by comparison with a standard instrument of Schaeffer and Budenberg, of Magdeburg. The gaseous mixture so obtained is passed through a receiver containing sulphuric acid into a pneumatic trough and collected over water; it is analysed from time to time in order to determine the composition of the residue. Fluctuations in the current by which the resistance furnace is heated can be compensated by interposed resistances, so that the furnace temperature does not vary beyond ± 5° C.

The results are indicated in the following table, which is a summary of 63 individual determinations:—

Temperature. C.	Velocity of Gas Current in c.c. per minute.	Catalyst.	Composition of the Gas.	NH_3 formed per cent.	Pressure p in Atmospheres.	$\sqrt{K} = \dfrac{p_{H_2}^{3/2} \cdot p_{N_2}^{1/2}}{p_{NH_3}} \cdot P$.
685°	48 0 to 4·8	Mn	0·765 H_2 + 0·235 N_2	0·896 to 0·849	49·6 to 49·1	1,796 to 1,875
809°	179·0 to 7·4	Mn	0·760 H_2 + 0 240 N_2	0·530 to 0·494	57·4 to 57 0	3,515 „ 3,802
809°	92·1 to 4·0	Mn	0·765 N_2 + 0·235 N_2	0 346 to 0·331	40·2 to 40 4	3,770 „ 3,939
836°	64·3 to 3·0	Mn	0·765 H_2 + 0·235 N_2	0·436 to 0·396	56·8 to 57·0	4,210 „ 4,721
876°	75 0 to 13·8	Pt	0 650 H_2 + 0·350 N_2	0·236 to 0·254	44 5 to 48·2	5,582 „ 6,280
920°	54·0 to 9·3	Pt	0·820 H_2 + 0 180 N_2	0·273 to 0·250	62·0 to 69·0	7,220 „ 7,813
920°	63 0 to 16·5	Pt	0·750 H_2 + 0 250 N_2	0·221 to 0·230	53 0	7,483 „ 7,790
920°	74·0 to 6·9	Pt	0·780 H_2 + 0·220 N_2	0 290 to 0·352	69·5 to 74·5	7,393 „ 7,728
1,000°	37·5 to 8 3	Pt	0·820 H_2 + 0·180 N_2	0·182 to 0·176	58·3 to 56·3	10,020 „ 10,260
1,000°	120·5 to 9·3	Pt	0·650 H_2 + 0·350 N_2	0·151 to 0·175	48·7 to 59·8	10,000 „ 10,970
1,000°	146·0 to 22·6	Pt	0·750 H_2 + 0·250 N_2	0·053 to 0·061	16·4 to 18·8	10,050 „ 10,100
1,040°	186·0 to 8·8	Pt	0·780 H_2 + 0·220 N_2	0·179 to 0·182	68·0	12,080 „ 12,270

In this table p represents the partial pressures of the individual gases, and P is the pressure in the furnace in atmospheres. The

catalysts which were used consisted of platinum foil and finely divided iron or manganese. The iron was obtained by reduction of ferric oxide in a current of hydrogen. The manganese which was used was prepared by Prellinger's [1] method ; this consists in electrolysing manganese sulphate with a mercury cathode, drying the manganese amalgam *in vacuo*, and then distilling it in a current of ammonia, with formation of manganese and mercury. The most favourable result—namely, 0·896 per cent. of NH_3—was obtained in the experiment at 685° C. and 49·6 atm. pressure with a manganese catalyst.

It is impossible to consider here the comparison of these figures with those obtained by thermodynamical calculations as in Jost's "Dissertation," and in the *Zeitsch. f. Elektrochem.*, **32** (1907), 521. The not inconsiderable differences in the results obtained by Haber and Le Rossignol,[2] and by Jost, are shown by the following table :—

Temperature.	Percentage of NH_3 by Volume at 1 Atm. Pressure. Haber–Le Rossignol.	Jost.
700° C.	0·0221	0·0174
750° C.	0·0152	0·0119
800° C.	0·0108	0·00867
850° C.	0·00906	0·00645
930° C.	0·00650	0·00427
1,000° C.	0·00481	0·00320

No further explanation of the reason why their results were different from those of Jost was supplied by the further determinations of Haber and Le Rossignol on the ammonia equilibrium carried out in 1907 to 1908 at high pressures.[3] But these results formed the basis for co-operation with the B.A.S.F.

At a later date F. Haber, S. Tamaru and Ch. Ponnaz, again determined the ammonia equilibrium at 30 atm. pressure,[4] studying the temperature interval from 560° to 950° C., and attaining equilibrium from opposite directions in certain cases. The results were once more in agreement with the former values of Haber and Le Rossignol. Experimental values obtained by Haber for the specific heat and heat of formation of ammonia were as follows :—[5]

rature.	Calculated specific heat.	Specific heat found experimentally.
309° C.	10·20	10·3
422° C.	11·00	11·0
523° C.	11·86	11·8

[1] *Monatsh. f. Chemie*, **14**, 353.
[2] *Ber.*, **40**, 2144.
[3] *Zeitsch. f. Elektrochem.*, **14**, 181, 513.
[4] *Ibid.*, **21**, 89 (1915).
[5] *Chem. Ztg.*, 1915, p. 24.

Temperature	Calculated heat of formation.		Heat of formation found experimentally.
0° C. .	10,950	..	10,950
466° C. .	12,840	..	12,670
503° C. .	12,940	..	12,700
554° C. .	13,063	..	12,900
669° C. .	13,255	..	13,150

F. G. Keyes and H. A. Babcock [1] redetermined the thermochemical constants of ammonia, but more particularly with regard to liquid ammonia, the specific heat in 15° C. calories being found to be :—

1·152 between 0 ° and 20° C. and
1·172 between 20° and 50° C.

E. B. Sudlam [2] found that the ammonia equilibrium was considerably affected by the presence of hydrochloric acid.

The further investigations of Haber and Le Rossignol were characterised by the use of still higher pressures and the choice of more suitable catalysts. In 1908 the work was already directed by technical considerations due to closer contact with the B.A.S.F. The important publication of Haber and Le Rossignol on the preparation of ammonia from its elements in the *Zeitsch. f. Elektrochem.*, vol. **19** (1913), pp. 53 *et seq.*, is an abbreviation of their report to the B.A.S.F. for the years 1909–10. Haber has himself given an interesting account of the evolution of this process up to the point when it was adapted for large-scale operations by C. Bosch and his co-workers.[3]

In the light of these two publications, we will give a short description of the fundamental scientific investigations on the basis of which the Haber-Bosch synthesis was evolved. In order to emphasise its economic importance we will summarise prices in 1909–10. At that date 1 kg. of ammonia in the form of ammonium sulphate had a value of about 89 pfg., whilst the nitrogen and hydrogen necessary for its production cost $2\frac{1}{2}$ pfg. and $17\frac{1}{2}$ pfg. respectively.

At the ordinary temperature and pressure nitrogen and hydrogen would combine almost quantitatively according to the equation

$$N_2 + 3H_2 \rightleftarrows 2NH_3,$$

could equilibrium be established, but, in practice, they cannot be made to react. At a bright red heat, on the other hand, it is easy to cause nitrogen and hydrogen to combine, but equilibrium is attained after the formation of very small quantities of ammonia. According to the laws governing equilibrium, a definite pressure and temperature can be found at which the yield of ammonia is the

[1] *Journ. Am. Chem. Soc.*, **39**, 1524 (1917).
[2] *Chem. Trade Journal*, December 15th, 1917.
[3] *Chem. Ztg.*, 1914, p. 742.

most favourable, starting from a gaseous mixture of 1 volume of nitrogen and 3 volumes of hydrogen. The proportion of ammonia obtainable at a given temperature rises approximately proportionally to the pressure of the gaseous mixture. According to the results of Haber and van Oordt, which we have already mentioned, the temperature should be reduced to 300° C. in order to obtain satisfactory yields. No catalyst is, however, known which will initiate the reaction at this temperature. In practice, therefore, no other way is open than the choice of a catalyst which will be highly active at as low a temperature as possible, and the raising of the pressure to such a point that the ammonia concentration at the end of the reaction is as high as possible. These are the principles of the modern synthesis of ammonia at high pressures. The working pressure and the choice of catalysts must be governed by technical considerations.

The lowest temperature at which the time of reaction and amount of catalyst attain practicable dimensions is about 500° C. Above 700° C. the equilibria are attained considerably more rapidly, but, on the other hand, the catalyst is then more easily damaged and the equilibrium is unfavourable. Theoretically the following yields of ammonia are approximately attainable :—

Temperature . .	500° C.	550° C.	600° C.	650° C.	700° C.	
100 atm. pressure .	11·0	7·0	4·5	3·0	3·2	per cent. NH_3 by volume.
200 atm. pressure .	18·0	12 0	8·0	6·0	4·0	,,

In small-scale experiments the ammonia may readily be removed from the reaction gases by liquefaction with a mixture of ether and solid carbon dioxide. The gases which return to the reaction furnace are used to pre-cool the fresh gases in a regenerator before entering into reaction.

The most important experimental results, which were all attained with a mixture of 1 volume of nitrogen to 3 of hydrogen, are contained in the following summary :—

	Excess Pressure in Atmosphere.	Temperature. C.	Gas Velocity in Litres per Hour.	Per cent. NH_3 in Effluent Gases.
Cerium, cerium-lanthanum, cerium-iron, cerium-manganese	50	700° to 800°	Variable.	0·19 to 0·33
1·3 gm. of a manganese preparation produced from manganese amalgam *in vacuo* (see above)	163	665°	6·0	3·30
	163	610° to 620°	6·0	2·60
Uranium obtained directly in the electric furnace, in a current of nitrogen and hydrogen, which crumbles spontaneously to a loose powder	190	about 600°	20·0	5·80 Duration 1½ hours.
	190	580°	3·0	7·00
	125	570°	3·2	5·65
	125	505°	25·7	6·54
	125	496°	9·5	9·10
Long period experiments . .	125	503° to 493°	2·0	11·00 to 11·90
Tungsten metal from the chloride .	Favourable results.			
Ruthenium	Not particularly advantageous, as it is very expen-			

Finely divided osmium proved to be a very good catalyst. Its activity increased during use for some time. After being used continuously for two and a half days, its activity had scarcely altered. In order to obtain as high a yield as possible per unit of time, 30 litres of gas were passed per hour at 610° C. and 169 atm. pressure, and the resulting gases contained 3·65 per cent. of NH_3. At 521° C., and a lower gas velocity more than 9 per cent. of NH_3 was obtained. At a dark-red heat and 175 atm. pressure, concentrations of ammonia of 8 volumes per cent. were easily obtained. In spite of its excellent effect, osmium could hardly have been used as a catalyst in technical practice, as the supplies of osmium are limited and its price is very high.[1] Other catalysts were, therefore, sought for, and were found in the form, for example, of molybdenum and iron, the latter being used industrially to-day in a specially prepared form. With ruthenium, ammonia concentrations of 11 to 12 volumes per cent. can be attained at less than 100 atm. pressure and 450° C., but ruthenium is even rarer and more expensive than osmium.

The experimental investigations were very detailed and were continued throughout many years; they greatly increased our knowledge of the behaviour of catalysts and catalyst poisons. A. Bernthsen [2] believes the negative results of former investigators who had worked on the formation of ammonia with catalysts consisting of base metals, to be largely due to the utilisation of catalysts and gases containing catalyst poisons. In the patent literature which will be discussed later, the regeneration and purification of the generated contact masses plays a large part. In a lecture given by C. Bosch [3] at the Eighty-sixth Meeting of the Deutsche Naturforscher und Ärzte in Bad Nauheim on September 20th, 1920, he explained all the difficulties which were encountered during the initial development of the high-pressure synthesis of ammonia since the B.A.S.F. made their first preliminary experiments in 1908. The work at very high pressures, which attained 200 atm. at temperatures of 500° to 600° C., constituted a new industrial development of a very adventurous character. The first large-scale experiments in which osmium was used as a catalyst were dramatically ended by an explosion of the contact plant. On closer investigation it was found that the plant had become quite brittle, and that the osmium had been completely oxidised to osmic acid, an indication that the gases could not have been free from oxygen. Serious difficulties were also

[1] *Zeitsch. f. Elektrochem.*, 1913, p. 69.
[2] *Zeitsch. f. angew. Chem.*, 1913, i., 10.
[3] *Chem. Ztg.*, 1920, p. 721; also A. Bernthsen, *Chem. Ztg.*, 1912, p. 1133; F. Haber, *Chem. Ztg.*, 1910, p. 345; 1913, p. 584; E. Herre, *Chem. Ztg.*, 1914, p. 317, 341.

encountered in practice when uranium was used. A catalyst was then sought for which could be used in technical practice, and for this purpose innumerable systematic experiments had to be carried out; the problem had then to be faced of discovering methods of preventing the hot gases from gradually destroying the iron walls of the apparatus. Extensive experimental arrangements had to be devised for this purpose, and a special workshop was erected for the production of high-pressure apparatus. The destructive action of hydrogen on steel and other metals was studied in detail for almost two years before success was attained in the construction of special apparatus with materials specially suited for the purpose, which was able to withstand the working conditions and ensure safe working. After many thousands of individual experiments, a satisfactory catalyst was finally found, consisting of iron mixed with certain definite materials and prepared in a suitable manner. Apart from the solution of these important problems, the manufacture of hydrogen had also to be carefully studied.[1]

The first technical experimental plant of the B.A.S.F. produced about 25 kg. of NH_3 daily at the commencement of 1911; in 1912 the production was increased to 1,000 kg. daily; in the summer of 1913 the large plant at Oppau commenced manufacture with a daily output of 30 tons of ammonia.

We will give a short description of the laboratory apparatus used in the original experiments of Haber, van Oordt, Le Rossignol and the B.A.S.F., as the large-scale plant was developed by Bosch and Mittasch taking this as a model.

The arrangement is readily comprehended.[2] A thin-walled iron tube of 9 to 13 mm. bore is wrapped in a layer of asbestos paper around which is a spiral of nickel wire, by means of which it can be electrically heated. Inside this iron tube there is a glass or quartz tube which contains the catalyst behind a constriction at the far end. The constriction of this tube is continued in the form of a steel capillary through which the reaction gases leave the furnace. The ammonia contained in these gases is removed either directly by cooling or by an absorption agent such as water or acid. The residual gases return into the circuit.

The whole contact apparatus just described, is enclosed in a steel high-pressure bomb. The interval between the reaction chamber and the inner wall of the bomb is filled with a heat insulating mass, and is maintained under high pressure.

The principle of this apparatus is indicated in the diagram

[1] F. Haber, *Chem. Ind.*, 1920, p. 350; *Chem. Ztg.*, 1920, p. 913.
[2] F. Muhlert, *loc. cit.*, pp. 122–123.

(Fig. 16), which is reproduced from an article by E. Herre,[1] and from a German patent application which was later withdrawn, namely, German Patent application 45,523/iv/12 g (1910), by the firm of Kunheim & Co., of Berlin. Any danger of bursting of the container is avoided by surrounding the reaction chamber by gas at the same pressure in an outer pressure chamber, the walls of which are suitably cooled.

Fig. 17 illustrates the small experimental plant which Haber used at the first public demonstration of his process before the Naturwissenschaftliche Verein at Karlsruhe on March 18th, 1910. *I* is the catalyst furnace corresponding to Fig. 16; *II* is the liquifier with

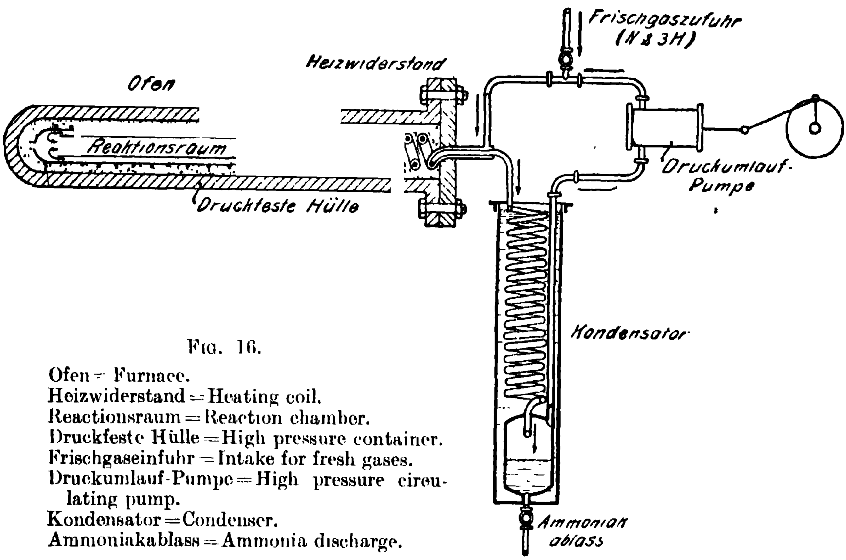

FIG. 16.

Ofen = Furnace.
Heizwiderstand = Heating coil.
Reactionsraum = Reaction chamber.
Druckfeste Hülle = High pressure container.
Frischgaseinfuhr = Intake for fresh gases.
Druckumlauf-Pumpe = High pressure circulating pump.
Kondensator = Condenser.
Ammoniakablass = Ammonia discharge.

heat exchanger and ammonia level gauge; *III* the high pressure circulating pump; *IV* is the intake for fresh gas; *V* the discharge valve for the ammonia; and *VI* a petcock which enables the ammoniacal contents of the gaseous mixture to be determined at any moment.

The patent literature of this subject is extremely voluminous, and patents still appear which show that experimental work has by no means ceased. Most of the patents are in the names of the B.A.S.F. or of Haber as proprietors, and they date from 1908 onwards.

After Haber and Le Rossignol had shown that it was actually possible to combine nitrogen and hydrogen to form ammonia at pressures of 150 to 200 atm. and at about 500° to 600° C. in presence

[1] Ullmann's "Encyclopædia," vol. i. (1914), p. 386.

German Patent 259,872 the carbides of the rare earth metals are recommended as catalysts.

The investigations of the B.A.S.F. were the first to explain the part played by certain materials as activators, which increase the efficiency of the ordinary ammonia catalysts.[1] The most favourable influence is exerted by the oxides and hydroxides of the alkalis, alkaline earth or rare earth metals ; on the other hand, all substances which are capable of introducing sulphur, selenium, tellurium, phosphorus, arsenic, boron or similar non-metals into the catalyst in any form are injurious (German Patent 249,447). The metals of the iron group are particularly susceptible to the effects of such activators and poisons. Whilst small additions of certain foreign metals may under circumstances exert a favourable influence, compounds of metals of low melting point, such as lead, tin, zinc or bismuth, readily reducible by hydrogen must be avoided (German Patent 258,146, and French Patent 425,099). The activators are either added directly to the finished catalyst mass, or mixtures of activator and catalyst in any form such as the oxides are prepared, and are then reduced after being fused (German Patent 254,437). According to German Patent 262,823, KNO_3 and similar substances also act as activators. It was also found that particularly valuable results are obtained with metallic mixtures in which certain constituents have an affinity for hydrogen, and others an affinity for nitrogen. For example, according to German Patent 286,430, ammonium molybdate is gently heated so that a portion of the ammonia is evolved. The porous granules which remain are soaked in a concentrated solution of palladium nitrate, until 20 per cent. of palladium nitrate is present, calculated in terms of the molybdate, and the mixture is then calcined in order to decompose the nitrate and reduced in hydrogen, or the mass is directly introduced into the contact furnace. Uranium nitrate may also be added to the palladium nitrate.

The action of activators [2] is ascribed by Bernthsen [3] to the fact "that the admixed materials dissolve in the oxides on heating, or are finely divided therein, and that, therefore, on subsequent reduction, a hardly perceptible network is formed within the metallic mass which effectively prevents shrinking of the surface and reduction in the catalytic activity." One may speak of positive or negative activators, the former being those which accelerate, and the latter those which retard the reaction.

The negative activators act as poisons. The action of such

[1] Bernthsen, *loc. cit.*
[2] Haber, *Zeitsch. f. angew. Chem.*, 1914, pp. 321–473; *Zeitsch. f. Elektrochem.*, **20**, 597 (1914); **21**, 89, 128, 191 (1915).
[3] *Loc. cit.*

contact poisons was already known from the study of the catalytic production of SO_3. The platinum contact used for that purpose is particularly susceptible to minute traces of arsenic, which probably causes the platinum to become covered with a vitreous non-volatile layer of a compound of As_2O_3 and SO_3. On the other hand, when sulphur trioxide is produced with iron oxide as a catalyst, the presence of arsenic is found to be advantageous. These examples showed how complicated catalytic phenomena could be,[1] but the study of the ammonia synthesis soon led to the recognition of the fact that in this case the conditions were still more complicated and the number of contact poisons very much larger. Apart from the substances enumerated in German Patents 249,447 and 258,146, certain carbon and certain oxygen compounds, such as SO_2, must be added. According to Bernthsen,[2] extremely minute quantities of such contact poisons suffice to reduce the action of the catalyst very considerably. Iron from iron oxide containing 1 part per 1,000 of Na_2SO_4 was found to be useless; the same result is caused by 0·1 per cent. of sulphur, and even 0·01 per cent. of sulphur lowers the activity very considerably. Very often traces of catalyst poisons were found to be fatal which could scarcely be detected by qualitative examination of the raw material.

In order to avoid interference by such contact poisons, catalyst masses must be prepared with the greatest care, and the reaction gases must be purified most scrupulously. Poisoned catalysts, which have become useless, may be revivified by heating them and the activators in oxygen or an oxidising atmosphere, according to German Patent 263,612. The nitrogen and hydrogen which are used must be absolutely free from contact poisons, such as phosphorus, arsenic, carbon monoxide and so on, before they enter the catalyst chamber (German Patent 254,344). According to German Patents 302,555 and 303,292, one part of sulphur per 1,000,000 exerts an unfavourable result.[3] Hydrogen is specially purified, as will be described below. Minute drops of lubricating oil, which tend to accompany the gases passing through the compressor, must be most carefully removed. Before they are allowed to enter the catalyst chamber the gases are, therefore, passed through filters, washed with suitable reagents, or passed at a high temperature over catalyst masses similar to those which are afterwards to be used in the high-pressure apparatus.

[1] G. Bredig, in Ullmann's "Encyclopædia," vol. vi. (1919), pp. 665–688; also R. Bauer-Wieland, "Reduktion und Hydrierung organischer Verbindungen" (Leipzig, 1918).

[2] *Loc. cit.*

[3] F. Muhlert, *loc. cit.*, p. 126.

According to A. Bernthsen,[1] many thousands of individual experiments were necessary before the subject of catalyst activity was thoroughly understood. The credit for this work, which was of extraordinary importance for the technical success of the process, is due to A. Mittasch.[1]

Although the foundations were thus laid for the practical working of Haber's ammonia synthesis, the equally important problem remained of discovering a safe and durable large-scale plant.

The problem of working on a large scale under the conditions required by the synthesis was so unheard of that most technologists took up a very sceptical attitude towards the undertaking.[2] The triumph of the B.A.S.F. was all the greater, when it ultimately achieved its aim after extremely difficult and tedious work lasting for several years, which is closely associated with the name of C. Bosch and his co-workers.

The large-scale plant is, in principle, identical with the laboratory apparatus which we have already described. The first descriptions were given in British Patent 17,591/1909, German Patents 235,421 and 152,275, French Patent 406,943, and Austrian Patent 45,010. The plant was first so arranged that the gas circulated continuously at high pressure. The reaction chamber, separator and circulation pump were connected in series similarly to the arrangement in Haber's demonstration apparatus. The ammonia which was produced was continuously separated as liquid by refrigeration. Its constituents have naturally to be replaced by fresh supplies of gas; the constituent gases circulate continuously through the whole plant. The plant was also so arranged that heat transference occurred between the ingoing and outgoing gases. It was found later, however, that the advantages of heat transference and of continuous circulation are relatively unimportant when working at pressures of 150 to 200 atm. and temperatures of 650° to 700° C. The direct production of liquid ammonia is no longer carried out, but this gas is removed as concentrated ammoniacal liquor by washing with water (German Patent 270,192).

Continuous working with high-pressure apparatus soon showed that under manufacturing conditions the gases attacked the walls of the reaction chamber so strongly[3] that these were ultimately completely destroyed. Further investigation[4] showed that steel containing carbon, which would otherwise be the most suitable material, loses carbon under the pressure and temperature conditions present

[1] *Loc. cit.*
[2] See Serpek, *Zeitsch. f. angew. Chem.*, 1914, p. 43.
[3] C. Bosch, *Chem. Ztg.*, 1920, p. 721.
[4] Bernthsen, *loc. cit.*

in the reaction furnace, in the presence of hydrogen, and thus completely loses its pressure-resisting qualities. Pure iron is also altered under such conditions, and is far too pervious to hydrogen.[1] German Patents 254,571, 256,296, 259,870, 265,295, 281,926, 291,582, 298,199, 306,333 ; French Patents 456,963, 458,218, 466,303 ; British Patent 29,260/1913 ; and U.S. Patent 1,202,995, mainly deal with descriptions of the precautions by means of which it has been possible to overcome these difficulties, so that the plant which is now used, although sensitive, ensures perfectly safe working. As already described in the case of the experimental laboratory arrangements, the reaction chamber is confined within a separate pressure chamber. The comparatively thin hot wall enclosing the reaction chamber is exposed to the same high pressure within and without ; the outer pressure chamber can be maintained at a lower temperature, and is, therefore, considerably more resistant.

The constructional material for the parts directly exposed to the hot gases may consist of nickel surrounded by iron, of iron free from carbon or a similar metal. Steel containing carbon, together with 18 per cent. of tungsten and 3 per cent. of chromium is also recommended. A surrounding atmosphere of nitrogen has proved particularly advantageous for the protection of the iron walls of the chamber which supports the pressure. Other investigations of the B.A.S.F. have shown that special steels containing little or no carbon are particularly suitable for the construction of such high-pressure containers. As long as sufficient quantities of the necessary auxiliary metals, such as chromium, vanadium, tungsten and molybdenum, are present, the apparatus retains its strength even at temperatures above 450° C., even after the carbon has been completely or partially removed in the form of gaseous compounds through the action of the hydrogen. Special steels containing 2 per cent. of chromium, together with 0·2 per cent. of carbon or 5 per cent. of tungsten and 5 per cent. of nickel are excellently suited for the construction of the hot high-pressure containers. It is now no longer necessary to use iron free from carbon, as these special steels can be used, with consequent simplification and reduction in price of the whole contact apparatus.

In the patents which we have so far described, nothing is said on the method of heating the contact chamber. The addition of a heating unit would complicate the apparatus considerably. Further investigation of the conditions showed that the heat liberated during the formation of ammonia is sufficient for the supply of the necessary quantity of calories if an adequate heat recovery system is provided (German Patent 259,870). When starting the process, air or other

[1] Mathesius, "Eisenhüttenwesen" (Leipzig, 1916).

gas containing oxygen is mixed with hydrogen and passed over the catalyst in the pressure chamber, where combustion ensues, and the actual synthesis is only started when the necessary temperature has been attained. In spite of satisfactory heat exchange, temperature fluctuations naturally occur during the synthetic manufacture of ammonia in the course of continuous practical working; these are similarly rectified by adding small quantities of air to the circulating mixture of nitrogen and hydrogen before its entry into the furnace.

We know from Bernthsen's [1] work that particular care must be taken not to add oxygen or air in large quantity, as at high pressures the explosive limit is very soon reached. This contingency is guarded against by special recording and alarm contrivances. The composition of the gases is also continuously controlled by analytical tests. Under these conditions, the above-mentioned method of auxiliary heating by the admixture of small quantities of air has to be carried out with great care or replaced by other indirect methods of preheating the circulating gas before its entry into the contact chamber.

In any case, the quantities of heat which it is necessary to introduce are extremely small, and the main work is comprised in the compression of the gases to the necessary high pressure. According to Haber [2] the power required for this purpose at 150 atm. pressure is not much more than ½ k.w.h. per kilogram of fixed nitrogen. The profit on the Haber-Bosch process is therefore mainly dependent on the production cost of the hydrogen. It is far less dependent on very cheap sources of power than the cyanamide or arc processes.

The extraordinarily detailed studies of the use of the most various catalysts have, on the whole, scarcely increased our knowledge of the method and mechanism of their action. One is inclined to assume that their action is dependent on the intermediate formation of unstable nitrides or hydrides. Numerous patents, therefore, deal with the suggestion of using such nitrides as catalysts (German Patents 246,554, 250,377, 259,648, 260,010, 259,647, 261,819). German Patents 246,554 and 265,294 deal with the alternate passage of nitrogen and hydrogen over a nitride. A working temperature of less than 600° C. is usually maintained, but it is advisable to add 1 to 3 per cent. of hydrogen to the nitrogen.

The present method of carrying out the Haber process is as follows: The stoechiometric mixture of nitrogen and hydrogen is introduced into the contact chamber after having been compressed to about 200 atm. pressure in three stages. Owing to the peculiarities

[1] *Loc. cit.*
[2] *Chem. Ztg.*, 1913, p. 584.

of the Haber process, it appeared desirable to depart from the form of autoclave commonly used and to replace it by tubular vessels with very thick walls on the lines of those used in the experimental apparatus. Similar forms of apparatus had been proposed by others, for instance, by C. E. Stromeyer, the engineer of the Manchester Steam Users Association,[1] and the high-pressure tubular autoclave of A. G. Kühnle, Kopp & Kausch, of Frankenthal. It was initially found necessary to build the contact furnaces of iron free from carbon, but high-pressure containers are now constructed of the special steels already referred to. The inner zone of the contact furnace is filled with the iron catalyst, the main features of the preparation of which are to be gathered from the patent literature, but the detailed composition of which is maintained as a strict secret. After the contact apparatus has once been brought to the reaction temperature, the heat evolved by the synthetic process itself maintains the necessary temperature ; the plant is so built that as complete a heat transference as possible is ensured. The actual reaction zone is surrounded by an outer chamber through which the constituent gases pass ; by this means the heat of the furnace is transferred to the gases, and the walls of the reaction chamber are simultaneously cooled and overheating is thus avoided. Moreover, the hot gases issuing from the contact furnace pass in counter-current to the cold constituent gases in the preheaters, so that here also an effective heat transference occurs. The effluent gases contain on the average 10 per cent. of ammonia when they leave the contact furnace. They are well cooled and then brought into contact with water whilst still under high pressure. A very pure solution of ammonia, containing 20 to 25 per cent., is thus obtained, which is withdrawn from the washers and stored in vats, despatched in tank waggons or further treated in the same works. The gases which escape from the high-pressure washers contain nitrogen and hydrogen only. If the proportions of these two gases are no longer correct, the composition is adjusted by addition of the necessary constituent, the quantities removed by formation of ammonia are replaced and the gases returned into circulation. A detailed description of the Oppau plant with sketch plans is to be found in *Chemical and Metallurgical Engineering*, 1921, vol. xxiv. pp. 305, 347, 391, "La Technique Moderne," 1920, p. 449, and *L'Industrie Chimique*, vol. viii, pp. 44, 86 and 122 (1921).

The Haber-Bosch synthesis of ammonia was realised in the form just described. Haber's great achievement consisted in the fact that on the basis of his own laboratory investigations and of the

[1] *Chem. Ztg.*, 1918, p. 311.

equally important and fundamental results of the work of Jost and Nernst at high pressure, he proceeded further at a time when the quantitative yields and the difficulties of the process appeared to be most discouraging. He was not content merely to investigate the equilibrium conditions, but with a definite object in view he endeavoured to accelerate the formation of ammonia by the action of suitable catalysts, pressures and temperatures, which were experimentally investigated, so that the synthetic methods might become commercially practicable. He was fortunate in finding associates in the B.A.S.F., and more particularly in C. Bosch, who spared neither trouble nor expense in adapting the process to large-scale technical conditions.

Apart from the patents already mentioned, the following, which were taken out by the B.A.S.F., are concerned with the Haber ammonia synthesis: German Patents 275,156, 277,526, French Patents 449,010, 466,003, British Patents, 1,161, 8,617, 9,842 and 25,259, all of 1913. Before considering the methods of further treatment of the ammonia which is obtained in this manner, we will discuss the methods of synthetic production of ammonia which have been patented or otherwise published by others, but before doing so, we wish to point out that the Haber-Bosch process is still the only one which has been used on a large industrial scale. The processes of de Jahn and the General Chemical Co. in America, of Maxted and Brunner, Mond & Co., Ltd., in England, and of Claude in France have so far not progressed beyond the experimental stage.[1]

E. B. Maxted [2] (British Patent 114,663/1917) succeeded in obtaining ammonia in proportions of over 1 per cent. at atmospheric pressure by cooling the reaction products very rapidly. A high temperature is obtained by injecting the mixture of nitrogen and hydrogen into an oxy-hydrogen flame or into a high-tension electric arc. Rapid cooling is obtained by burning the flame under water. It is not clear why nitrogen and hydrogen should unite at such high temperatures as occur in these experiments, for at such temperatures ammonia is no longer stable. Attempts to obtain iron nitride from finely divided iron and nitrogen at 100 atm. pressure and 500° to 700° C. did not lead to the formation of even a trace of the product. Further, experiments with iron nitride obtained by other means showed that under the given conditions it would be impossible to obtain iron nitride from its elements. M. Guichard and his fellow-workers [3] wrote on the synthesis of ammonia on the basis of their own

[1] This is no longer the case.—TRANSLATOR.

[2] *J. Soc. Chem. Ind.*, **37**, 105 (1918); *Chem. Zentralbl.*, 1919, ii., 491; *Chem. Ind.* 1918, No. 13/14 "Dokumente."

[3] *Bull. Soc. encour. ind. nationale*, **132**, 71 (1920); *Chem. Zentralbl.*, 1920, iv., 467.

experiments. They experimented with a series of catalysts and erected a small experimental plant which produced 3 kg. of NH_3 hourly. General information on the synthesis of ammonia at high pressure is also given by J. Catala.[1]

The Société Générale des Nitrures of Paris use zinc or zinc alloys (German Patent 250,085) or tungsten (German Patent 254,934) as catalysts in the synthesis of ammonia. They mention a temperature of 500° to 800° C., and state that the catalyst should have as large a surface as possible, but the constituent gases need not necessarily be present in the proportion of 1 to 3. It should be noted that, according to German Patent 258,146 of the B.A.S.F., zinc is a contact poison. Much work has been published by the Centralstelle für wissenschaftlich-technische Untersuchungen G.m.b.H., of Neubabelsberg, which claims ruthenium as a catalyst in German Patent 252,997. At a pressure of 175 atm. the effluent gases are said to contain 20 per cent. of NH_3 by volume. In German Patent 286,666 an apparatus is described consisting of a pressure vessel of iron, enclosing a thin-walled well-fitting tube of aluminium, which in turn encloses a similar thin tube of iron poor in carbon. If this apparatus is exposed to pressure the iron and aluminium tubes are pressed against the walls of the iron vessel, forming a tight protective coating, as the iron is impermeable to nitrogen and the aluminium to hydrogen. Silver behaves similarly to aluminium (German Patent 278,958). In the course of a continuous experiment lasting 14 days, on a mixture of 85 per cent. of hydrogen and 15 per cent. of nitrogen at 150 atm. pressure in an iron tube lined with silver, no hydrogen losses were detected. The silver also resists the action of ammonia, which is not the case with aluminium. According to German Patents 286,853 and 290,877, molten Wood's metal is filled into an outer high-pressure container into which the inner reaction chamber is inserted. The intermediate layer of Wood's metal prevents the gases from diffusing to the walls of the high-pressure container. The carrier for the catalyst usually consists of magnesia or magnesium carbonate of which 10 to 20 times the weight of the catalyst is used. Further experiments by the "Centralstelle" have shown that pure chromium oxide, obtained by igniting pure chromic acid, is a still better carrier. According to German Patent 288,496, the chromium oxide is soaked in an aqueous solution of a salt of the metal which serves as catalyst, and is then dried in a stream of pure nitrogen and hydrogen. Chromium oxide is said to enable a yield to be obtained which is 10 to 20 times as great as that obtained with other carriers, such as uranium oxide, asbestos, cerium oxide, and so forth. According

[1] *Chem. Ztg.*, 1914, p. 429.

to German Patent 289,105, the action of magnesia or magnesium carbonate as a carrier is quite distinctive. Compounds of the platinum metals, such as ruthenium, rhodium and iridium chlorides, which exert no catalytic action when introduced alone into the contact chamber, are converted into very good catalysts when dispersed on 10 to 20 times their weight of MgO or $MgCO_3$. In the same manner the efficiency of bodies which are themselves catalysts, such as potassium rutheniate, can be considerably increased. In order to prepare a catalyst from ruthenium chloride and magnesia, one may, for example, precipitate the ruthenium from an aqueous solution of its chloride by magnesia or some other alkali, mix the precipitated and washed product, whilst moist, with 10 times its weight of MgO, and dry the preparation in a stream of nitrogen and hydrogen.

In German Patent 272,638 N. Caro recommends a contact substance prepared from soda-lime or potash-lime to which iron, titanium or vanadium are added. According to German Patents 275,343, 275,663, 277,054, 283,447, and French Patent 453,207, F. Hlavati ionises a mixture of nitrogen and hydrogen by means of electric sparks before passing it over the catalyst. According to Hlavati, the most active contact material contains 48·1 parts by weight of titanium and 195·2 parts by weight of platinum. Larger yields of ammonia were regularly obtained when the metals were present in the proportions of their atomic weights than when they were present in any other proportions. With an equiatomic mixture of titanium and platinum, almost double the yield of ammonia was obtained than was obtained with one containing equal parts by weight. Hlavati worked at various temperatures, but found that at high temperatures the fluctuations in the yield were not so large as low temperatures. According to German Patent 276,986 Kunheim & Co. attain concentrations of ammonia of $1\frac{1}{2}$ to 2 per cent. by volume by the use of cerium nitride at about 100 atm. pressure and a gas velocity of 60 litres per hour with a catalyst space of 4 c.c. only. In German Patent 281,317 J. Wolff claims the interaction of CO, N, and steam.

In German Patents 285,698 and 286,719, and French Patent 460,859, Farbenfabriken vorm. Fr. Bayer & Co. give detailed information as to a catalyst which they obtain from the ferri- or ferro-cyanides of the alkali or alkaline earth metals by heating these with as little access of air as possible, for example, in a covered crucible, or in a current of gas free from oxygen, and then passing nitrogen and hydrogen over the decomposition products which are so produced. For example, potassium ferrocyanide is heated at 600° to 700° C. at

the ordinary pressure in a stream of hydrogen, the greyish-black product is placed in a catalyst chamber and a mixture of nitrogen and hydrogen is then passed over it at 150 atm. pressure and 430° C. Concentrations of ammonia of 15 per cent. by volume are thus said to be continuously obtained. A still more efficient catalyst is obtained by heating barium ferrocyanide at high pressures whilst passing over it the nitrogen and hydrogen mixture ; the catalyst is formed at 300° C. with simultaneous production of ammonia, the formation of which at 430° C. and 180 atm. pressure is so energetic that a concentration of 17 to 18 per cent. by volume is continuously obtained.

In German Patent 289,795 A. Classen claims to combine nitrogen and hydrogen directly by heating the gaseous mixture in presence of catalysts at temperatures of 25° to 90° C. under the influence of dark electric discharges. As an example, he gives the following directions for the preparation of suitable catalysts. Gelatose is added to a solution of chloroplatinic acid in concentrated aqueous solution and the platinum is reduced with hydrazine hydrate or other reducing agents. The suspension of colloidal platinum so obtained is shaken up with suitable quantities of a carrier such as asbestos or is evaporated and dried. In order to obtain chromium, ferro-chromium, ferrosilicon, chrome nickel or other metallic substances in a very finely divided form, they may be etched with acids and bases, and then treated with a sufficient quantity of 60 per cent. gelatose solution in a ball mill with steel or granite balls for several days or weeks ; Plauson's colloid mill may also be used with advantage. In this manner the gelatose is converted into a voluminous foamy mass which takes up the finely divided metal. By adding neutral materials, a mixture is obtained which forms suitable contact masses after drying and igniting. When steel balls are used the ignited mass includes iron oxide, which acts both as a carrier and as a catalyst. The oxides of nickel, uranium and tungsten behave in a similar manner. In German Patent 310,623 H. Harter and H. Braun claim the use of iron, including electrolytic iron, as a catalyst for the high-pressure synthesis in the form of rods or tubes which have been produced in the usual manner by drawing, rolling or casting. The iron is first so treated that iron, ferrous and ferric oxides are all present. Such conditions are chosen for treatment that hydrogen peroxide can be formed, the production of which is accelerated by the addition of active metals. The contact material is filled into a relatively narrow tube through which the gaseous mixture is led, and several such tubes are united in a wider tube. In this process the velocity of the reaction gases is said to be considerably

increased, as the bore of the individual tubes is very small. When using low pressures a high yield of ammonia is obtained and the plant is thus simplified, and wear and tear is relatively small. (See also German Patents 276,718, 276,953.) H. Hampel and R. Steinau [1] proposed to combine nascent hydrogen with nitrogen. In order to achieve this, they lead the vapours of ammonium chloride over iron at a high temperature, and obtain the following reaction :—

$$\text{I.}\quad Fe + 2NH_4Cl = FeCl_2 + 2NH_3 + H_2.$$

If nitrogen at high pressure is also present, this combines with the hydrogen to form ammonia :—

$$\text{II.}\quad 3Fe + 6NH_4Cl + N_2 = 3FeCl_2 + 6NH_3 + 2NH_3.$$

Thus an additional 2 molecules of ammonia are produced apart from the six which are introduced into the process in the form of ammonium chloride. The ferrous chloride is treated with aqueous ammonia according to the equation :—

$$\text{III.}\quad 3FeCl_2 + 6NH_3 + 6H_2O = 3Fe(OH)_2 + 6NH_4Cl.$$

The NH_4Cl is returned into the cycle according to Equation I., and the ferrous hydroxide is converted into metallic iron by reducing gases, and can also be used according to Equation I. In spite of the statement that the wear and tear of the apparatus is very slight and that a gaseous mixture containing 98 to 99 per cent. of NH_3 is obtained at 50 atm. pressure and 300° C., the process has never been carried out on a large scale. Seventy-five per cent. of the NH_3 return into the cycle at each circulation and the rest is available for other purposes. J. Fischler [2] considers that iron nitride is presumably formed as an intermediate product in the process according to Equation I.; this assumption is scarcely to be reconciled with the previously mentioned difficulty in producing iron nitride.

Matignon uses tungsten or its alloys as catalysts for the synthesis of ammonia, and in U.S. Patent 1,089,241 he claims to use this material at 25 to 50 atm. pressure and 300° C. Peacock uses iron hydrides (U.S. Patent 1,092,167). There is a whole series of patents in the names of F. W. de Jahn and the General Chemical Co., of New York. According to U.S. Patents 1,141,947 and 1,141,948, pumice is soaked in cobalt nitrate solution and then reduced with hydrogen. The carrier prepared in this manner is coated with metallic potassium or sodium in an atmosphere of hydrogen, and is then heated to 300° C. in a current of ammonia gas until the weight remains constant. The catalyst must be stored in an atmosphere of dry ammonia gas. It is active at 80 to 90 atm. pressure. The cobalt may be

[1] *Chem. Ztg.*, 1918, p. 594.
[2] *Ibid.*, 1919, p. 11.

replaced by nickel, iron or molybdenum, or by equivalent quantities of magnesium, cerium, boron, titanium, uranium or silicon. According to U.S. Patent 1,143,366, 175 gm. of dry pumice, purified with hydrochloric acid, are introduced in small pieces into an aqueous solution of 257 gm. of nickel nitrate. The pumice is then dried and heated to 550° C. When no further vapours are evolved, the material is heated for 11 hours to the same temperature in a stream of hydrogen until no further water is formed. Twenty grammes of metallic sodium are then added, and it is dispersed throughout the mass in a molten condition. The atmosphere of hydrogen is then replaced by an atmosphere of dry ammonia and the preparation heated to 450° C., by which means nitrogen is absorbed. The catalyst is preserved in an atmosphere of ammonia. In an atmosphere of nitrogen and hydrogen it is active at 525° to 540° C. and at 80 to 90 atm. pressure yields concentrations up to 4·5 per cent. of NH_3 by volume. U.S. Patent 1,159,364 claims the use of pumice and metallic sodium only at 550° to 600° C. and 85 atm. pressure, by which means 5 per cent. of NH_3 by volume is obtained, whilst U.S. Patent 1,159,365 claims the use of metallised pumice (see 1,141,947/8) as a carrier and sodium or potassium as a surface layer only. For the catalyst the following are used: cobalt as nitrate, manganese, titanium, cerium, uranium, silicon as chloride, and elementary boron. The components of the mixtures are to be used in atomic proportions. These catalysts give a concentration of 4·5 per cent. of NH_3 by volume at 520° to 540° C. and 80 to 90 atm. pressure.

In U.S. Patents 1,090,874 and 1,119,534 M. Pier claims as catalyst the use of ruthenium salts, more particularly of potassium rutheniate $K_2RuO_4(+H_2O)$, the per-rutheniate $KRuO_4(+H_2O)$, and the hydroxide $RuO(OH)_3$. At 450° C. and 80 atm. pressure, a gas is obtained containing 11 to 12 per cent. of NH_3 by volume, whilst at 175 atm. 20 per cent. by volume of NH_3 are obtained. In U.S. Patent 1,120,960 C. C. Meigs claims the combination of nitrogen and hydrogen under the influence of the electric discharge. According to U.S. Patents 1,167,280 and 1,184,839, C. Ellis utilises washed cerium oxide, obtained as a by-product in the manufacture of gas mantles, containing as impurities the oxides of lanthanum, yttrium and so forth, which exert a favourable effect; he melts this and disintegrates it in a rotary furnace by the sudden action of a jet of hydrogen at high pressure, and absorbs it in granulated cocoanut charcoal, which has previously been washed with dilute hydrochloric acid and water and heated to about 300° C. in hydrogen. This catalyst is said to be very active at 60 to 80 atm. and temperatures of 350° to 450° C. (see also U.S. Patent 1,083,703).

In British Patent 103,148/1916 F. Perry claims to produce synthetic ammonia by passing Mond gas, which may be mixed with steam, over heated iron or heated coke at 650° to 700° C. G. Claude's synthesis at high pressure has already been mentioned in the section on the French nitrogen industry (see also British Patent 130,086/1917. It is said that a company has recently been formed in Kobe, Japan, with the object of working this process on a large scale.[1] G. Claude describes his method in detail in *Compt. rend.*, vol. clxx, No. 3 (January 19th, 1920),[2] pp. 174–177 ; he points out that under the conditions of the German process, namely, a temperature of 536° C. and a pressure of 200 atm., the gases have to pass through the cycle very many times, attaining a concentration of 10 to 12 per cent. of NH_3 at each cycle, in order finally to convert 80 to 90 per cent. of the constituents into ammonia. G. Claude [3] first investigated to what extent the concentration of ammonia is altered if the pressures are greatly increased, and obtained in this manner the following equilibrium concentrations :—

C.		Per cent. NH_3.
536° at	200 atm. .	12·5 (Haber-Bosch conditions).
536° ,,	400 ,, .	21·0
536° ,,	600 ,, .	28·5
536° ,,	800 ,, .	36·0
536° ,,	1,000 ,, .	41·0
607° ,,	1,000 ,, .	30·0
672° ,,	1,000 ,, .	20·0
740° ,,	1,000 ,, .	14·0

At 1,000 atm., as at 200 atm., the optimum temperature is between 500° and 700° C. Below 500° C. the reaction velocity is too small. Under the most favourable experimental conditions, 6 gm. of ammonia can be obtained hourly per gramme of catalyst. G. Claude proposes to pass the gases 3 times through the catalyst at 1,000 atm. pressure, in order to obtain quantitative conversion. The power absorbed by the increased compression is said to be more than compensated by the greater cheapness of the smaller catalyst units, and the ease with which they are manufactured and supervised. At each phase the conversion is 25 per cent. of NH_3. In the concentrated mixture the ammonia can be liquefied by cooling with water only, whilst the gas from the Haber-Bosch process, which is not so concentrated, requires to be cooled to — 40° C. for this purpose. Whilst the B.A.S.F. no longer isolate the ammonia as liquid NH_3, but absorb it completely by water, Claude still proposes to separate the ammonia in the liquid form. He also proposes to combine this

[1] *Chem. Ztg.*, 1920, p. 804.
[2] *Chem. Zentralbl.*, 1920, ii., 524 ; *Chem. Ind.*, 1920, p. 128.
[3] *Chem. Ztg.*, 1920, p. 592.

process with the ammonia soda process by separately crystallising sodium bicarbonate and ammonium chloride from the mother liquors by finally cooling to + 5° C. Claude produces the necessary degree of refrigeration by evaporation of the liquid ammonia which he obtains by the high pressure synthesis. In this manner the necessity for distilling the ammoniacal liquor, as in the Haber-Bosch process, is avoided, and the whole of the ammonia from the ammonia soda process is obtained as ammonium choride without any necessity for distillation of the ammonia. The removal of the ammonia from the reaction gases of the Haber-Bosch process results in a pressure drop of 10 to 20 atm., which must be restored by further compression. Claude, on the other hand, passes his nitrogen-hydrogen mixture through a very small number, usually 3, of contact units, at 1,000 atm. pressure, and about 500° to 600° C. After each unit the gas, which contains 25 per cent. of NH_3, is freed from the bulk of this by cooling with water, by which means the ammonia is separated in the form of liquid without any loss of pressure. The recovery of argon as a by-product thus becomes simpler, and the whole power economy is better.

This is the position as claimed by Claude in the publication just referred to. Technical results have, however, not hitherto proved favourable, and it is not very evident why a process should become better and safer in working through the use of such extremely high pressures. H. Hampel and R. Steinau [1] criticised even the Haber-Bosch process in the following terms: "The difficulties are more particularly of a technical order, namely, the extremely complicated and expensive plant, the depreciation of which is, moreover, rather excessive. Economic working is only possible by continuous careful technical supervision extending to all details." These remarks appear to be much more applicable to Claude's synthesis at 1,000 atm. pressure.

Details of the plant are described, for example, in British Patents 130,086 and 130,087/1917. The combination with the ammonia soda process is described by G. Claude [2] also by L. Hamburger.[3] In German Patent 321,617 R. W. Wallace and E. Wassmer describe the use of magnesium, aluminium or titanium as catalysts (see also French Patent 466,102 by B. Lepsius).

The high-pressure synthesis results in the production of free ammonia; this is not in itself a fertiliser, but must be converted into a suitable salt before it is practically available for the farmer.

[1] *Chem. Ztg.*, 1918, p. 594.
[2] *Chem. Zentralbl.*, 1919, iv., 450.
[3] *Ibid.*, 1920, iv., 279.

The B.A.S.F. has, therefore, devoted much attention to ammonia fixation processes. Here also chemical and engineering difficulties were met with of a similar order to those which had to be overcome in carrying out the ammonia synthesis itself. C. Bosch discussed these questions both at the Twenty-fourth General Meeting of the Deutsche Bunsengesellschaft [1] at Berlin on April 8th to 10th, 1918, and also at the Eighty-sixth Annual Meeting of the Deutsche Naturforscher und Ärzte [2] (Bad Nauheim, September 19th to 25th, 1920).

In his first address C. Bosch first denies the French claims to priority, and then turns to the question of the conversion of ammonia into fertilisers. Unexpected difficulties often occur when apparently simple processes are converted into large-scale operations. Very slight alterations in the method of working often influence the mechanism of the reaction when many hundred tons of product have to be prepared. It is generally assumed that large-scale manufacture is cheaper than small-scale production. Some of the experiences of the large-scale nitrogen industry point, however, in the contrary direction. The endeavour to replace human labour by machinery necessitates the erection of extensive and expensive plant which is usually soon seen to require improvement. Changes are then made during the operation of the process and losses very often occur. Therefore, the advantages of large-scale, as compared with small-scale manufacture, are often only apparent after working for a very considerable time. More particularly during the War, one was only too frequently requested to operate processes on a large scale which could not be explored step by step. In such cases, difficulties accumulated. When erecting new plant the engineer is usually more concerned with the mechanical than with the chemical nature of the questions involved. It is, therefore, extremely important that the chemist should be acquainted with the principles of engineering science, as it is very difficult for the engineer to acquire the necessary chemical insight. The practical establishment of the high-pressure ammonia synthesis was only possible by the close co-operation of engineering, chemistry and physics.

The first ammonium sulphate saturator, in which free sulphuric acid was directly neutralised by synthetic ammonia, was intended for the production of 100 to 120 tons of the salt per twenty-four hours, whereas in coke-oven plants before that time, saturators of 10 to 20 tons output daily were the largest which had been constructed. "Now, whereas in coke-oven plant the ammonia had been absorbed

[1] *Zeitsch. f. Elektrochem.*, **24**, 361–396 (1918).
[2] *Chem. Ztg.*, **1920**, p. 721–732.

quantitatively, the absorption was found to be less in the large plant, which was built on the lines of the saturators used in the gas industry.[1] It was found that the leaden bells of the saturator were corroded and perforated, also that the phosphor-bronze parts of the pumps were destroyed, occurrences which had not previously been observed. The suggestion that possibly coke-oven ammonia contained substances which protected lead proved not to be correct ; explanations were only found when the behaviour of lead was investigated with acid, alkaline and neutral solutions of ammonium sulphate. It was found that the disturbances were due to local alkalinity of the ammonium sulphate solution. The consequence of the increased size of the cells, necessary for the higher output, was that these worked less regularly, larger quantities of ammonia could escape, and the ammonium sulphate solution became ammoniacal. This disadvantage was avoided by the establishment of better circulation by means of stirrers. The attack of the phosphor-bronze portions of the pumps was due to a somewhat higher temperature of the circulating liquid, and it was possible to avoid this by suitable and sufficiently moderate cooling."

In order to render Germany independent of the importation of foreign pyrites, attempts were made to utilise the sulphur of the gypsum deposits, even though at a financial loss. The problem was, therefore, attacked of utilising the gypsum which is found in enormous quantities in the Muschelkalk district of the Neckar. The large installation at Neckarzimmern, in which attempts were made to recover sulphur by the interaction of gypsum and coal in vertical kilns worked extremely uneconomically. The loss due to the formation of carbon oxysulphide was very heavy, and the depreciation of the kilns was so high that the newly erected works, which had involved the expenditure of very heavy capital, had to be closed at the very moment when the working had improved slightly. An indirect process proved to be more suitable. Gypsum was smoothly converted into ammonium sulphate and calcium carbonate by passing ammonia and flue gases into its aqueous suspension, a small amount of sulphuric acid being first added in order to start the reaction. All that was then necessary was to filter and evaporate the solution when the ammonium sulphate was obtained in a perfectly pure condition. " In this way it is possible to utilise the flue gases and simultaneously to avoid the damage which these cause to agriculture in the neighbourhood. In order to avoid losses of ammonia these have subsequently to be washed with a little water, and a special method of filtration had to be evolved. The tendency

[1] *Zeitsch f. angew. Chem.*, **1918**, iii., 242 ; *Chem. Zentralbl.*, **1919**, ii., 411.

of calcium carbonate to form solid incrustations in the plant, and so to cause stoppages, is overcome by working in sufficiently large vessels. A third process is the combination of ammonia with sulphurous acid to form ammonium bisulphite and oxidation of this to sulphate. This reaction appeared to be impossible on a large scale, as the decomposition of the bisulphite is of an explosive character, but at a low temperature, and with the addition of sulphur or selenium as a catalyst, the reaction could be carried out successfully." Ammonia can also be fixed by superphosphates. "Ammonium chloride is an ammonium salt which has not yet been used extensively in agriculture, but which may ultimately be so used, and can be manufactured by a modified ammonia soda process. The only other fertiliser which has played an important part in agriculture, apart from ammonium sulphate, is sodium nitrate, and endeavours had to be made to produce this from ammonia. Ammonia was first oxidised to nitric acid and the platinum catalyst was successfully replaced by iron. The manufacture of synthetic nitrate was greatly increased in order to replace Chile nitrate, which was unobtainable. The plant for this purpose at Oppau, which started operations in May, 1915, was only able to operate successfully after many months of difficulty. Now that the initial difficulties have been overcome, these works represent a real technical asset. Synthetic nitrate is purer than Chile nitrate. Nitrates can be obtained without the use of soda by manufacturing ammonium nitrate. The main difficulty of this manufacture is in the evaporation of the ammonium nitrate solution, as the wrought iron of the evaporating pans is converted into a brittle form by the action of the hot concentrated solution. For some unknown reason wrought iron is particularly liable to this change. The ammonium nitrate liquors are, therefore, evaporated in cast-iron pans, but a white product is only obtainable under special conditions. When mixed with suitable additions, such as sodium or potassium chloride, ammonium nitrate serves as an excellent substitute for Chile nitrate; these mixtures are neither hygroscopic nor explosive; they are readily spread and are now being produced on a very large scale under the names of calcium ammonium nitrate, gypsum ammonium nitrate, bonemeal ammonium nitrate, potassium and sodium ammonium nitrate, and ammonium sulphonitrate. The fertilising value of calcium nitrate is very high, but unfortunately it is very hygroscopic. If, however, its four molecules of water of crystallisation are replaced by urea, it furnishes a useful fertiliser. The manufacture of urea is simple. When ammonium carbonate is heated under pressure to 140° C., a large amount of urea is formed. It should, however, be noted that

the heat of reaction of the production of carbamate is very considerable. Difficulties also occur with regard to metals which can be used in the apparatus, as lead and silver are the only metals which are unattacked by carbamate.

The agricultural chemist of the B.A.S.F., Dr. Frese, held a lecture at Stettin on October 20th, 1915, to the Agricultural Association of the Randow district on "The Ammonia Process of the B.A.S.F. and the Fertilisers manufactured by that Firm." He stated that the B.A.S.F. then manufactured the following new fertilisers (partially on a very small scale, for experimental purposes) :—

		Per Cent. N.
Urea, pure	containing	46·60
Urea nitrate, pure	,,	34·15
Ammonium chloride . . .	,,	26·42
Sodium nitrate	,,	16·50
Urea-calcium nitrate, Ammonium nitrate, Urea superphosphate . . .	,,	35·00

The B.A.S.F. has established an agricultural research station near Ludwigshafen for the testing of these fertilisers ; it is furnished with all the most modern arrangements, and the potting shed holds 1,000 individual pots. Advisory agricultural stations at Ludwigshafen, Munich, Stuttgart, Cologne, Cassel, Münster, Hanover, Kiel, Berlin, Halle-a.-d.-S., Stettin, Dresden, and Breslau serve for propaganda purposes and carry out field experiments in all parts of Germany.

At the meeting already referred to, the lecturers, Dr. Frese and Dr. Störmer, of the B.A.S.F., stated that the Government was at first unable to subsidise the B.A.S.F., and that it was only anxious to obtain a nitrogen monopoly in order to render its cyanamide plant capable of competition. After the fact became known that the cyanamide industry was being heavily subsidised, the B.A.S.F. approached the Government with a request for a guarantee of 30,000,000 marks (£1,500,000). In return, the company promised to deliver 300,000 tons of ammonium sulphate by a definite date. The Government, which had not been in communication with the company up to that time, made no reply for a considerable period, and then enquired by telegram whether the B.A.S.F. could increase the suggested delivery of ammonium sulphate by a further 150,000 tons. As a telegraphic reply was required within one hour, the negotiations fell through, it being impossible to come to such an important decision in such a short time. In consequence the Oppau works were first built with the company's own capital.

Circumstances then compelled the Government to alter its course of action, and considerable capital was placed at the disposal of the B.A.S.F., more particularly in order to erect the works at Merseburg-Leuna.

According to a special communication by the B.A.S.F., the Oppau works[1] produced 25 to 30 tons of ammonia daily, starting in the summer of 1913; during the War this output was increased to an annual production of 70,000 tons of ammonia. The Merseburg-Leuna works started operations in 1917, and the output of these will shortly amount to 200,000 tons of NH_3 annually.[2] When completed both works together will produce 300,000 tons of combined nitrogen annually. The daily production of Merseburg-Leuna in 1918 was 400 tons of NH_3.[2] At that time about 100 tons of 100 per cent. nitric acid was produced daily at Oppau.[2] Since that time the ammonia oxidation plant at Oppau, which uses an iron oxide catalyst, has been increased to such an extent that 500 tons of HNO_3 can now be produced daily, leaving a sufficient surplus of ammonia to supply the Höchster Farbwerke and other works. At the close of 1920, the ammonia works at Oppau and Leuna, together with the gypsum quarries, were converted into a special limited company with a capital of 500,000,000 marks (£25,000,000), the participation of the B.A.S.F. being 124,095,000 marks (£6,204,750); the style of this company is "Ammoniakwerke Merseburg-Oppau G.m.b.H. in Ludwigshafen-a.-Rh."

The processes carried out at Oppau and Leuna may now be described. The gypsum-ammonium sulphate process is being operated both at Oppau and Merseburg. The B.A.S.F. owns its own gypsum quarries at Niedersachswerfen, in the south of the Harz not far from Nordhausen, which supply the Merseburg works. Difficulties were at first encountered in developing the process, and have already been mentioned. Rotary filters were adopted for filtration of the calcium carbonate sludge and proved very satisfactory. In the middle of 1919 the daily production at the Leuna works was about 200 tons of sulphate, but this was to be increased to 1,000 tons daily. The gypsum-ammonium sulphate process is characterised by the perfectly neutral reaction of the product. Ammonium bicarbonate is manufactured on a fairly large scale, and has found application, for example, as baking powder, for which purpose it is superior to the ammonium carbonate formerly used. Ammonium chloride is obtained directly from common salt by the ammonia soda process.[1] Great possibilities are expected from the manufacture of urea on account of the high

[1] Direct information from B.A.S.F.
[2] *Zeitsch. f. angew. Chem.*, 1919, ii., 749.

nitrogen content of the product and the absence of non-nitrogenous constituents. A plant is being erected for its manufacture from ammonia and carbon dioxide.

The catalytic oxidation of ammonia [1] is exclusively carried out with an iron-oxide catalyst. The nitrous gases so obtained are treated with water and with solutions of soda in large reaction towers, producing nitric acid or sodium nitrate. The nitric acid, which is obtained, of approximately 50 per cent. strength, is concentrated with the help of sulphuric acid in a special plant.

Ammonium nitrate would constitute an ideal fertiliser were it not so deliquiescent, causing storage difficulties. As a fertiliser, it shows both the immediate action of nitrate nitrogen and the more gradual action of ammoniacal nitrogen. Its high nitrogen content is a favourable characteristic from the standpoint of transport. On the other hand, the farmer is accustomed to the use of the old fertilisers—namely, Chile nitrate containing 16·47 per cent. of N when pure, and ammonium sulphate containing 21·2 per cent. of N when pure—and estimates his requirements on this basis. For these reasons exception has been taken to the use of pure ammonium nitrate as a fertiliser, and this has led to admixture with other substances which decrease the nitrogen content and also the very marked hygroscopic character. It therefore appears on the market mixed with bonemeal, gypsum or calcium carbonate. Potash-ammonium nitrate, soda-ammonium nitrate and ammonium sulpho-nitrate were later produced by interaction with potassium chloride, sodium chloride and ammonium sulphate respectively. These mixtures are neither explosive nor hygroscopic. The farmer does not take readily to these new mixed fertilisers. As already mentioned, he prefers fertilisers of uniform chemical character the proportions of which can be regulated by him according to the circumstances and the character of the soil. The manufacture of ammonium chloride, ammonium nitrate and ammonium nitrate mixed fertilisers has been described in *Chem. Ztg.*, 1921, p. 557. According to this description, the concentrated ammonium nitrate liquor is mixed at Oppau with potassium chloride or ammonium sulphate in shallow mixing pans. The paste which is so produced passes along a screw conveyor, belt conveyors and bucket conveyors to rotary drying ovens, and thence to two storage sheds each 100 m. long. Technical ammonium sulphonitrate contains rather more ammonium sulphate than corresponds to the formula :—

$$2NH_4NO_3 \cdot (NH_4)_2SO_4.$$

[1] C. Bosch., *Chem. Ztg.*, 1920, pp. 721–722.

Potash ammonium nitrate contains 40 parts of potassium chloride to 60 parts of ammonium nitrate. Numerous experiments showed that mixtures containing less than 60 per cent. of ammonium nitrate were no longer explosive. Ammonium sulphonitrate was broken up in the storage shed by blasting. The explosive character, which is only shown by pure ammonium nitrate with a powerful detonator (2 to 3 gm. of fulminate) is almost absent in the mixed fertilisers. Unfortunately they cake on storage through absorption of water. At 7.30 a.m. on September 21st, 1921, a terrible explosion occurred in the ammonium sulphonitrate stores at the Oppau works, involving 4,500 tons of ammonium sulphonitrate; 600 lives were lost, and great damage was done to property throughout a radius of several kilometres. It is not clear whether the catastrophe was due to especially powerful detonation or to spontaneous decomposition of the stored material;[1] according to Deputy Brey, the latter cause was indicated in advance by discoloration of the white salt and a temperature rise to 50° to 60° C.[2] The German Reichstag at once formed a "Parliamentary Commission for the Investigation of the Oppau Catastrophe," and invited numerous experts to attend the sittings. The event also caused much comment in the daily press.[3] The "Nitrogen Committee" of the Imperial Ministry of Food and Agriculture published an opinion based on expert reports, that no danger was involved to the farmer when using ammonium nitrate mixed fertilisers and storing them on a small scale. It also stated, however, that it should never be blasted in the course of agricultural operations.

The Badische Anilin und Soda Fabrik now supplies the following nitrogenous fertilisers:—

(1) Ammonium sulphate, B.A.S.F., containing about 20·5 per cent. N.

(2) Sodium nitrate, B.A.S.F. (German nitrate), containing about 16 per cent. of N, free from plant poisons.

(3) Ammonium sulphonitrate, B.A.S.F., containing about 27 per cent. of total nitrogen, about 8 per cent. of which is nitrate nitrogen and 19 per cent. ammoniacal nitrogen.

(4) Potash ammonium nitrate, B.A.S.F., containing about 16 per cent. of N, half of which is ammoniacal and half nitrate nitrogen, and 25 to 27 per cent. of K_2O.

The very considerable saving in freight charges which may be accomplished is indicated, for example, by comparison between

[1] *Chem. Ztg.* (1921), 937, 965; *Chem. Ind.* (1921), 406; *Metallborse* (1921), 2092; *Techn. i. d. Landw.*, 1921.

[2] "Proceedings of Reichstag," September 28th, 1921.

[3] *B. Z. am Mittag*, September 26th, 1921.

ammonium sulphate and urea; 1 ton of the former compound contains about as much nitrogen as half a ton of the latter.

The high output of fixed nitrogen from the works at Oppau and Leuna is a main feature of the German nitrogen industry, the productive capacity of which is discussed by P. Ehrenberg[1] in an instructive lecture on "The Nitrogen Requirements of Wheat Crops and their Supply," read before the Eighty-sixth Meeting of the Deutscher Naturforscher und Ärzte in Bad Nauheim on September 19th to 25th, 1920. It is as follows:—

	Tons of N.
1918	92,000
1919	115,500
1920 . . . . approx.	134,500

Ehrenberg discusses the unfortunate decreases in the demand which have been noticeable in the German nitrogen industry since the middle of 1920. That these are not due to any lack of useful possibilities of application is shown by the fact that, according to a rough calculation the six main crops, namely rye, wheat, summer barley, oats, potatoes and hay, including the stubble left in the ground, absorbed approximately 1,000,000 tons of nitrogen in 1918. "As further losses and deficient utilisation, due to weather and other circumstances, must be included, we arrive at a consumption of $1\frac{1}{3}$ million tons of nitrogen for the six main crops for harvests, which were comparatively small owing to the consequences of the War." This nitrogen requirement must be supplied from the following sources: atmospheric precipitation, activity of soil bacteria, animal manure, nitrogen products from the distillation of coal and fixed nitrogen fertilisers. The difficulty in disposal of these latter is all the more deplorable as the efficiency of nitrogenous fertilisers has long been definitely determined, and it is known that 1 ton of nitrogen in readily available form is able to produce 20 times its weight of wheat or rye grain, a still larger quantity of oats or barley grain, 200 times its weight of potatoes, and 300 times its weight of root crops. According to Ehrenberg, the reasons why the agricultural demand has slackened are, that unfortunately fertilisers are still considered as materials only to be bought at certain seasons, that the prices of the nitrogenous and other fertilisers do not directly correspond to the sale prices of many main crops (thus, for example, the increase in price of wheat up to 1920 was only eight-fold, in which the premium for early thrashing is included) and finally that compulsory production, labour conditions, and the general economic situation have exercised an important influence.

[1] *Chem. Ztg.*, 1920, p. 722.

"The decreases in sales are so considerable that the works are faced with the necessity of storing their output of fertilisers, which is expensive and often quite impossible, and the fear is increasing that this most important factor in increasing the crops will not be fully available for our future harvests." If the German harvest decreases, a correspondingly larger amount of food must be imported at unfavourable rates of exchange, for the very unsatisfactory food supply of the German nation renders the further reduction of the quantity of food quite impossible. The Versailles Peace Treaty has considerably reduced the harvest area of the German Empire to the east and west, and it is therefore necessary to endeavour to increase the production of the remaining area as much as possible. From this standpoint, the decrease in sales of nitrogenous, potash and superphosphate fertilisers is a very grave symptom. Ehrenberg therefore recommends Government action in order to ensure a decrease in the price of fertilisers.

The provision granted by the Agricultural Committee of the Reichstag, to allow the export of 25,000 tons of fixed nitrogen [1] free of export tax, must therefore be greeted with very mixed feelings. On the one hand, the increased production so obtained may actually be the first step in stabilising and reducing inland prices for fertilisers, but on the other the utilisation of this 25,000 tons in Germany would enormously reduce the necessary imports of foodstuffs from abroad.

The great difficulty in disposing of the products was also referred to at the General Meeting of the Bayrische Stickstoffwerke in 1920. Although efforts to improve the situation had been made in many official quarters, and Hermes, the Minister for Food Supplies, stated at the third meeting of the National Agricultural Council on July 22nd, 1920, that the necessary reduction in the price of food could only be attained by a reduction in the sale prices of fertilisers and foodstuffs, no improvement was discernible at the commencement of 1921. The spring sales in 1921 showed a slight improvement. At the end of 1921 the demand could be described as normal. A more rapid disposal of the product was not even achieved in the middle and at the end of 1920 by the information that the Nitrogen Syndicate would make an allowance of 40 pfg. per 100 kg. for the August delivery in 1920 in lieu of storage, and that all deliveries until October 31st would be subject to a reduction in price corresponding to 8 to 10 per cent. interest on the invoice amount up to that date.

[1] *Zeitsch. f. angew. Chem.*, 1920, ii., 331. For example, the exports of ammonium sulphate in 1920 were:—26,093·5 tons (valued at 126,657,000 marks), of which 222·8 tons went to France, and 13,690·5 tons to Holland.

The attempts of the Ministry of Food and Agriculture to reduce the prices of fertilisers have so far been without success. On the other hand, the output should be greatly increased in order to neutralise the increase in the price of coal, of wages, and of raw material, and so to stabilise prices and prevent a further increase in the same. Without support from their reserves, which was granted for many years in spite of very high prices, several large works would have had to stop manufacture.

Although the situation of the German nitrogen fixation industry at the commencement of 1921 reflected the very serious economic condition of Germany, it must be remembered that the main difficulties were partly of a seasonal character and partly due to the uncertainty of the general economic relations of the country. The few statistics which have been given here show how very large the demands for nitrogen really are. Production and sales must be further adjusted and the economic situation must become healthier before a real and permanent improvement in the nitrogen fixation industry can be expected. If the food requirements of the whole nation render it necessary, the Government will have to reduce the prices of fertilisers artificially by means of subsidies, for, as Ehrenberg says, it is better and more just "to spend half a milliard or more in order to pay our own countrymen, rather than to spend four or five times the amount abroad." The objection is sometimes made that the fixation of nitrogen uses up such a large quantity of German coal that it would be better to purchase Chile nitrate, use ammonium sulphate from coke ovens and gas works only, and to use the coal thus saved for the development of other industries, more particularly of those which furnish exports; this objection should also be considered from the wider standpoint already mentioned. It is true that the principles underlying the objection are to some extent correct, but, taking everything into consideration, it is abundantly clear that it is better to utilise domestic coal in order to manufacture fertilisers in the country, and utilise these latter in improving the food supply, rather than to import food from abroad at the present unfavourable rate of exchange. It must also be remembered that during the War the erection of nitrogen fixation works was necessitated by circumstances quite different from those of to-day, and that we are making a virtue of necessity by utilising the present large works to the utmost extent for peace purposes.

At the 86th meeting of the Deutsche Naturforscher und Ärzte at Bad Nauheim (September 19th to 25th, 1920), Max Rubner [1] emphasised the great physiological importance of nitrogen for the

[1] *Chem. Ztg.*, 1920, p. 723.

production of food of men and animals, and J. Bueb [1] discussed in detail the future development of the ammonia market.

Large quantities of ammonium chloride (23 per cent. N) sodium nitrate (16 per cent. N), ammonium sulpho-nitrate (27 per cent. N), and urea (46 per cent. N), were placed at the disposal of the German Agricultural Society by the B.A.S.F. for the purposes of large agricultural experiments. The German Agricultural Society asked farmers to carry out such experiments,[2] and pointed out the excellent results which had already been obtained by various agricultural stations. Ammonium chloride is used in exactly the same manner as the sulphate. Synthetic nitrate and ammonium sulpho-nitrate are used in exactly the same manner as Chile nitrate. Urea fertilisers can also be used for all field crops, but the higher nitrogen contents and the texture of the soil must be taken into account. The lighter and more porous the soil, the less fertiliser should be used in autumn for winter crops. Not more than one-third of the total intended quantity of fertiliser should be used in the autumn, except on porous soil of better quality, on which the whole quantity may safely be applied at that season. Nitrogenous fertilisers should be harrowed in shortly before sowing.

The methods adopted by the B.A.S.F. in order to interest farmers in large-scale experiments and to introduce their new fertilisers appear to be very well chosen.

The Ammoniakwerke Merseburg, commonly known as the Leuna Works, have been erected since 1916 within the boundaries of five small country parishes, and at present employ about 18,000 workers. The five communities have united in order to cope with the heavy responsibilities which have arisen, more particularly with regard to police, and in the middle of 1920 the combined communities employed thirty officials with a total salary bill of 360,000 marks. The expenses for buildings, schools, poor rate, and so forth, have also grown greatly, and the B.A.S.F. have shouldered a portion of the responsibility. Light railways and settlements have completely altered the general character of the district. The Leuna Works cover an area of about 6 × 1 km. The storage capacity for ammoniacal liquor is about 25,000 cu. m. In 1919 only about 200 tons of nitrogen per day were fixed in the form of concentrated (20 per cent.) ammonia solution, although a greatly increased output could have been attained. When the works are complete, the output is intended to be 200,000 tons of combined nitrogen yearly. The gypsum-ammonium sulphate plant has been working since about the beginning of May,

[1] *Chem. Zentralbl.*, 1920, ii., 236; "Technik. in der Landwirtschaft." 1920, p. 306.
[2] "Agricultural Review," *Magdeburgische Zeitung*, August 5th, 1920.

1919, at which date it produced 50 tons daily. There is a satisfactory supply of coal for the evaporation plant, boilers, and so forth, as the works possess their own pit close at hand.

As already mentioned, at the end of 1920 the ammonia works at Oppau and Leuna were withdrawn from the control of the Badische Anilin und Soda Fabrik, A.G., and taken over by an independent limited company with a capital of 500 million marks. The share capital of this company is divided among the eight firms of the Interessengemeinschaft in the proportions of their general quota. The output at Oppau is to be increased to 100,000 tons of N, and that at Leuna to 130,000 tons, and finally to 200,000 tons of N yearly.[1]

A. Sander [2] published an important communication on the history of the gypsum-ammonium sulphate process, from which it appears that the decomposition of ammonium carbonate with gypsum for the production of ammonium sulphate was already carried out industrially more than 100 years ago in Austria by the K.K. Salmiakfabrik Nussdorf in 1807–1809. In 1910 the use of the process in coke ovens and gas works was suggested by the Société Industrielle de Produits Chimiques of Cuise-Lamotte in German Patent 253,553. The B.A.S.F. found during their experiments that although calcium sulphate or gypsum readily reacts with solutions of ammonium carbonate to form ammonium sulphate and calcium carbonate, considerable difficulties are met with in endeavouring to separate the fine sludge of calcium carbonate from the ammonium sulphate solution, and in the complete recovery of the ammonium sulphate from the sludge (see German Patent 270,574). Complete separation was only effected by the use of rotary filters, such as are used in the gold-mining industry (German Patent 281,174). The calcium carbonate sludge covers the filter with a uniform, porous layer, which retains its porous qualities when subsequently washed. In this manner the ammonium sulphate is removed practically completely from the calcium carbonate sludge with small quantities of water. Rotary filters consist of drums into which the liquid is filtered by means of a pressure difference between the inside and the exterior.

It was found later that if impure gypsum of the quality usually found is used, filtration becomes impossible. By igniting the gypsum at 300° C. or over, filtration is much facilitated. Granulated or powdered gypsum is therefore ignited in rotary furnaces (German Patent 300,724). In this manner the ammonium sulphate solution

[1] *Chem. Ztg.*, 1920, p. 844.
[2] *Ibid.*, 1919, p. 661.

the necessary quantity of solid urea into a concentrated solution of phosphoric acid of about 50 per cent. strength, and heating. The product is filtered and a crystalline salt which is easily dried is obtained by cooling and inoculation if necessary. Excess of phosphoric acid must be carefully avoided. Interesting double compounds of urea and calcium nitrate, which can be used in a drill and are not hygroscopic, are described in German Patent 295,548. Such double compounds are obtained by intimately mixing 1 molecular proportion of calcium nitrate with 4 molecular proportions of urea and evaporating to dryness. The necessary quantity of urea may also be dissolved in a concentrated solution of calcium nitrate, on which the double salt crystallises out on cooling. German Patent 299,284 describes products obtained from urea or urea nitrate and superphosphate, which are quite dry and readily spread when fresh. They only become moist on long storage under certain circumstances. This disadvantage may, however, be overcome by treating the product with gaseous ammonia until it no longer shows acid reaction (German Patent 299,855). Ammonia may also be used in the form of ammonium salts of volatile acids, such as the carbonate, and dried air may be passed over the products. German Patent 299,942 is an extension of the one just mentioned, whilst German Patent 308,659 claims the addition to mixtures of urea and superphosphate of earthy, sandy, or carbonaceous material, such as finely divided soil, ground pebbles, fine sand, kieselguhr ashes, peat litter, ground coke, and so forth. In this way the mixture is maintained in a dry condition. The acid and moisture are absorbed, so that the final products can readily be spread.

U.S. Patent 1,173,550 of C. Bosch and the B.A.S.F. deals with the preparation of urea from ammonium carbonate by heating in a closed vessel and distilling the reaction products at temperatures not exceeding 80° C. The production of urea is almost quantitative, and the unchanged ammonium salts are readily recovered.[1]

According to German Patent 323,656, the amides of the alkali and alkaline earth metals are obtained by passing dry ammonia into solutions of the alkali or alkaline earth metals in anhydrous caustic alkalis at 275° to 300° C.

The above pages will have made it clear how important a part sulphuric acid still plays in the fixation of ammonia. It is therefore not surprising that other inventors and firms apart from the B.A.S.F. are, and have been, active with regard to the utilisation of gypsum, magnesium sulphate, and so forth, for the manufacture of sulphur and of sulphuric acid. Among the most recent

[1] German Patents 294,793, 295,075, 301,751, 303,929 of the B.A.S.F.

patents for the utilisation of gypsum, we can only mention here German Patents[1] 299,034, 300,715, 300,762, 301,712, 301,791, 303,233, 303,333, 303,922, 304,231, 305,103, 313,122, 318,221 and 319,651. The Neckarzimmern plant of the B.A.S.F. was a failure, and the Walbeck and Bernburg Works of the Kriegschemikalien A.G. were closed, as they proved to be unprofitable; the rotary furnace plant of the Farbenfabriken vorm. Fr. Bayer & Co. in Leverkusen had great difficulties to contend with, but now works quite smoothly. The various processes for the utilisation of the sulphur contents of coal gas have not yet achieved success,[2] so that in this field we are only at the beginning of future developments. These processes will certainly be of some importance in the future; coke ovens and gas works will then possibly obtain ammonium sulphate partially from the sulphur and the nitrogen in the coal, and the ammonia will be partially oxidised to nitric acid and converted into ammonium nitrate or mixed fertilisers. The process of the B.A.S.F. already described of converting ammonium sulphate into ammonium bisulphate also renders the use of the former compound possible in many cases in place of sulphuric acid—for example, for the decomposition of phosphates.

Initially it appeared to be simpler to use kieserite or the corresponding crude potash salts rather than gypsum for the production of sulphur or sulphuric acid. Very little more has, however, been achieved in this direction (German Patents 330,716, 307,042, 307,752, 312,775). H. Hiller[3] has scientifically investigated the process claimed in German Patent 256,400, according to which the sulphur dioxide in furnace gases is converted into sulphuric acid by blowing in air in presence of aluminium hydroxide, and has obtained very favourable results. The absorption can be carried out with gases, whether rich or poor in SO_2, by working in counter-current. In any case, flue gases represent an enormous reserve of sulphur dioxide.

So far the only practically successful process of replacing sulphuric acid from pyrites is that of the Farbenfabriken vorm. Fr. Bayer & Co. and the gypsum-ammonium sulphate process, which has been developed not only by the B.A.S.F., but also by others. According to German Patent 299,752, of the Chem. Industrie A.G. and Fr. Wolf, of Bochum, ammonium sulphate can be obtained from gas liquor, gypsum and carbon dioxide with simultaneous production of hydro-

[1] See Annual Reports, *Chem. Ztg.*, 1913, No. 110; 1915, No. 118 *et seq.*; 1916, p. 337; 1919, No. 131 *et seq.*, also *Chem. Ztg.*, 1920, p. 390; *Chem. Zentralbl.*, 1919, iv., 1109; German Patent 298,552.

[2] *Chem. Ztg.*, 1920, p. 742.

[3] *Zts. Ver. Gas. u. Wasserfachm.*, 7, 310 and 321 (1917); *Zeitsch f. angew. Chem.*, 1918, ii., 331.

gen sulphide. For example, 200 kg. of finely ground crude gypsum, containing 77 per cent. of $CaSO_4$, are mixed with 201 litres of gas liquor, containing 19·2 per cent. of NH_3, and 200 litres of water in a pressure vessel at 50° C.; carbon dioxide is then introduced at an excess pressure of ½ to 2 atm., and the whole is left for 5 hours. The reaction is then complete, and after driving off any liberated hydrogen sulphide the contents of the autoclave may be evaporated to recover ammonium sulphate or may be returned to the cycle in order to be further enriched. C. Matignon [1] has published certain particulars on the manufacture of ammonium sulphate from gypsum. According to this article, in 1864 Margueritte called attention to the fact that the chemical process

$$(NH_4)_2CO_3 + CaSO_4.2H_2O = CaCO_3 + (NH_4)_2SO_4 + 2H_2O$$

could be appreciably accelerated by the addition of a small quantity of calcium chloride. N. Basset and Tucker also started from gypsum, but their proposals never attained any practical importance.[2]

A whole series of patents are concerned with the fixation of ammonia by means of magnesium salts. When ammonia and magnesium chloride interact, the magnesium is partially precipitated, and a double salt is formed containing about 21 per cent. of ammonium chloride, 37 per cent. of magnesium chloride, 42 per cent. of water, and only 5·5 per cent. of nitrogen, which is therefore of no use as a fertiliser. Even if it is partially dehydrated, the contents of nitrogen are only increased 9 to 10 per cent. According to German Patent 292,174 H. Precht treats ammonium magnesium chloride as follows: 100 parts of the double salt are dissolved, for example, in 55 parts of boiling water; 30 to 40 per cent. of the ammonium chloride crystallises out on cooling. On concentrating the mother-liquor, the original double salt crystallises out, and a solution is finally obtained containing magnesium chloride only. In German Patent 292,209 the Kaliwerke Grossherzog von Sachsen A.G. and K. Hepke claim the absorption of ammonia by magnesium chloride liquors in absorption towers. In German Patent 292,218 H. Precht claims the decomposition of magnesium sulphate by ammonia in a special manner, so that the formation of the double salt, ammonium magnesium sulphate, is avoided as far as possible. Excess of ammonia, high concentration and long duration of the reaction favour the further decomposition of the double salt with formation of magnesium hydroxide and ammonium sulphate. The production of this

[1] *La Techn. moderne*, **8**, 350 (1914); *Chem. Ztg.*, 1915, "Repertorium," p. 73.
[2] German Patents 268,497, 270,532, 279,953; U.S. Patents 1,052,797, 1,072,840; French Patent 427,065.

double salt is further dealt with by H. Precht in German Patent 294,857, according to which he obtains it from 264 parts by weight of ammonium sulphate and 95 parts by weight of anhydrous magnesium chloride according to the equation :—

$$MgCl_2.6H_2O + 2(NH_4)_2SO_4 = 2NH_4Cl + (NH_4)_2SO_4.MgSO_4.6H_2O.$$

If the theoretical quantity of the magnesium salt is added, the double salt is almost completely precipitated as a fine crystalline powder. If the solution is heated, large crystals are obtained on cooling in short columns or thick plates of the monoclinic system, isomorphous with potassium magnesium sulphate. After the mother-liquor has been somewhat concentrated, ammonium chloride crystallises out. Ammonium magnesium sulphate is comparatively insoluble (20 parts in 100 parts of water), is not hygroscopic, and forms a very suitable plant food. Potash salts containing magnesium chloride are usually employed instead of pure magnesium chloride. In German Patent 295,509 H. Precht describes a process of decomposing ammonium magnesium chloride by ammonia. For example, he dissolves 100 parts by weight of the double salt in 100 parts by weight of water at the ordinary temperature, and adds 90 parts by weight of ammonia solution of sp. gr. 0·91. After about 10 hours the separated magnesium hydroxide, containing 8·38 parts by weight of magnesia, is separated from the double salt. As this latter originally contains 15·5 per cent. of magnesia, 54·1 per cent. of the original magnesium chloride has been decomposed. By increasing the excess of ammonia and the pressure, the same degree of decomposition can be attained in a very much shorter time.

According to German Patent 306,354, Salzwerke Heilbronn A.G. obtain ammonium chloride by passing steam and ammonia or ammoniacal gases over chlorides either fused or at a temperature of over 150° C. The reaction is assisted by the presence of carbon dioxide, powdered iron, iron oxide, alumina, and so forth.

In the *Gesammelten Abhandlungen zur Kenntnis der Kohle*,[1] H. Niggemann describes his experiments on the absorption of ammonia in concentrated magnesium chloride solutions. On passing a current of ammonia and air into a solution of 50 gm. of crystallised magnesium chloride in 50 c.c. of water at 90° C., magnesia commences to precipitate in about half an hour. When the solution was saturated with ammonia, 40·5 gm. of crystallised magnesium chloride was still present in solution. The filtrate contained 0·25 gm. of free ammonia and 1·709 gm. of fixed ammonia. When ammonia and carbon dioxide are led in simultaneously, magnesium carbonate is

[1] 1917, i., 289 ; *Chem. Zentralbl.*, 1919, ii., 615.

precipitated at once. The reaction appears not to be technically applicable for the absorption of ammonia.

In a detailed communication [1] H. Hampel discusses the production of potassium nitrate and ammonium sulphate from crude potash salts. He bases his work on the following equations, including the gypsum ammonium sulphate process and the formation of hydrochloric acid from magnesium chloride :—

(1) $MgSO_4 + CaCl_2 = MgCl_2 + CaSO_4$.
(2) $CaSO_4 + 2NH_3 + CO_2 + H_2O = CaCO_3 + (NH_4)_2SO_4$.
(3) $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$ and
(4) $MgCl_2 + H_2O = MgO + 2HCl$.

Hampel proposes to utilise the sulphuric acid radicle of magnesium sulphate for the fixation of ammonia and production of ammonium sulphate. It is impossible to effect this by a reaction similar to that of equation 2, as magnesium carbonate, $MgCO_3$, is never completely precipitated from solutions of ammonium salts and sometimes not precipitated at all. Crude potash salts containing sulphates are recommended as the most suitable raw material. The products obtained would then be magnesia, ammonium sulphate and potash salts, which can readily be further treated.

The manufacture of the gaseous components which is so important for the practical application of the Haber-Bosch process will be discussed independently later.

Supplement, 1921–1924.

Articles of General Interest.—Very many important articles on the subject have appeared, for example, by L. Cambi (*Giorn. Chim. Ind. Appl.*, ii., 309 (1920)), R. S. Tour (*Journ. Ind. and Eng. Chem.* **12,** 844 (1920) ; **13,** 298 (1921)), P. Firmin (*Ind. Chim.*, **9**, 147), A. Sander (*Zeitsch. Kompr. u. flüssiger Gase*, **22,** 1, 29, 41 (1922)), and J. M. Graham (*Journ. Ind. and Eng. Chem.*, **14**, 791 (1922)). There are many more articles on catalysts (*L'Engrais*, **35**, 305, 398 (1920) ; *Chem. and Met. Eng.*, **26**, 493, 555, 588, 647, 683 (1922) ; *Journ. Ind. and Chem. Eng.*, **12**, 289). Patent activity is mainly associated with the names of Duparc, Urfer, Clanty, the Nitrogen Company, Hlavati, Norsk Hydro, Metallbank, Greenwood, Tate, etc., and is mainly concerned with catalysts (British Patents 140,061/1920, 140,060/1920, 163,046/1921, 168,902/1920, 143,550/1920 ; Swiss Patents 93,808, 94,219 ; German Patents 326,928, 328,945, 299,751, 300,741, 340,753, 347,696, 342,622, 343,320 ; Norwegian Patent 35,049 ; French Patents 525,504, 532,066, 533,085, 538,155 ; Austrian Patents 89,039, 88,519 ;

[1] *Chem. Ztg.*, 1919, pp. 634–635.

Dutch Patents 5,861, 6,007, 6,350; U.S. Patents 1,388,448, 1,417,952 (*Journ. Ind. and Eng. Chem.*, **12**, 287, (1920)). A synthesis by electronic bombardment is suggested in *Chem. Ztg.*, 1073 (1921); 97 (1922); and by nitrogen reduction at platinum cathodes of large area in *Helv. Chim. Acta.*, 246 (1922). A survey of new apparatus is given by O. Kanock (*Chem. Apparat.*, **9**, 2, 15 (1922)); there is an article on the fixation of ammonia by gypsum in *Chem. Trade Journal*, **68**, 562 (1921). Vapour pressure tables for ammonia are published by Bergstrom, Altenkirch and others (*Journ. Phys. Chem.*, **26**, 358 (1922); *Zeitsch. ges. Kälteindustrie*, **28**, 173, 1921; *Phys. Ber.*, **3**, 239). Baly and Duncan maintain the existence of active and inactive forms of ammonia in *J. Chem. Soc.*, **121**, 1008 (1922). The preparation of thio-urea from ammonia and carbon disulphide is described in *Journ. Amer. Chem. Soc.*, **42**, 2072 (1920); German Patent 234,012.

The Haber Bosch Synthesis of Ammonia in Germany.—There are articles dealing with this subject broadly by Guichard (*Gas Journal*, **151**, 139 (1920)), Oster Jones (*Chem. and Met. Eng.*, **22**, 1071 (1920)), Tour, *loc. cit.*, **26**, 245, 307 (1922), and Hydegger (*Bull. Féderat. Ind. Chim. de Belge*, 187 (1922)). O. Herstad describes foreign attacks on the Haber patents (*Zeitsch. f. angew. Chem.*, 563 (1923)). The Oppau plant is described in detail in *Chem. and Met. Eng.*, **24**, 305, 347, 391 (1921); *L'Ind. Chim.*, viii., 44, 86, 122 (1921); *La Technique Moderne*, 449–460 (1920).

The ammonium sulphonitrate explosion at Oppau on September 21st, 1921, gave rise to a whole series of articles (*Chem. Ztg.*, 1034, 965, 1085, 1188 (1921); *Monit. Scientif.*, **5**, 11, 225 (1921); *Met. Gas.*, **42**, 12 (1922); *Metallbörse*, 107, 155 (1924); *L'Ind. Chim.*, viii., 390 (1921); *Rev. Prod. Chim.*, **24**, 589 (1921); *Chem. Ind.*, 635 (1923)). The Parliamentary Commission of Enquiry of the Reichstag which was formed on September 28th, 1921, issued its summarised report on December 21st, 1923 (Kast, *Chem. Ztg.*, 133 (1924)). The actual cause could not be determined with certainty. No blame could be attached to the administration of the works. The manufacture is in itself not dangerous, any danger being confined to blasting. Garaix read a paper before the Soc. des Ingenieurs Civiles de France on the economics of the Haber process.

The following patents of the B.A.S.F. deal with the preparation of gaseous mixtures and catalysts, and with methods of manufacture: German Patents 306,302/3, 338,828, 299,283, 304,341, 305,001, 334,975, 337,568; U.S. Patent 1,386,760. The ammonia which is manufactured serves for the production of urea by heating with carbon dioxide under pressure in presence of catalysts according to German Patents 295,075, 294,793, 295,389, 332,679, 350,051, 332,680,

301,279, 332,114, 308,569, 332,117, 333,671, 351,130, 372,262 of the B.A.S.F. Production of ammonium sulphate with the use of gypsum and otherwise is dealt with in German Patents 299,621, 333,117, 336,767, 352,978, 304,344, 310,141 ; *Zeitsch. f. angew. Chem.*, i., 45, 441, 457, 498 (1921) ; and the production of ammonium chloride mixed fertilisers in German Patents 326,619, 325,074, 301,674, 306,334, 307,112, 336,100, 350,630, 355,037, 354,956, 310,601, 336,876 ; British Patents 145,036/1921, 145,037/1921, 144,659/1920.

The French Synthesis by Claude and Associates.—The B.A.S.F. produce ammonia at a pressure of 200 atm., obtaining 13 per cent. of NH_3 in the exit gases. Claude, on the other hand, produces ammonia at 600 to 1,000 atm. and 550° C., attaining concentrations of 40 per cent. (*Compt. rend.*, **169**, 649, 1039 ; **170**, 274 ; C. Fermenti, *Giorn. Ind. Appl.*, ii., 312 (1920)). The most recent articles by Claude (*Compt. rend.*, **172**, 442 (1921) ; **174**, 157, 681 (1922) ; *Chim. et Ind.*, **3**, 5–8 ; *Acad. des Sciences*, **16**, 1 (1922) ; *Rev. Gen. des Sciences pures et appl.*, **32**, 534 (1921)), and his patents (British Patents 150,744/1920, 161,195/1921 ; French Patents 519,648, 520,464, 501,147, 524,576, 525,927, 523,689, 523,869, 536,770, 537,195 ; German Patents 341,230, 358,021 ; Swiss Patents 90,307, 95,233 ; Norwegian Patent 33,323) deal for the most part with compressors, heat exchangers, the cooling of the walls of the pressure vessels, the fixation of ammonia by the ammonia-soda process, etc. They are supplemented by British Patents 177,494/1922 and 177,777/1922 of the Soc. Chimique de la Grande-Paroisse Azote et Produits Chimiques, which describe a suitable steel for the high-pressure apparatus, containing, for example 0·018 per cent. Si, 0·09 per cent. S, 0·098 per cent. C, and 0·93 per cent. Mn. The economics and so forth and the process itself are described in detail in *Chem. Age*, **5**, 665 ; *J. Soc. Chem. Ind.*, **40**, R. 420 ; *Zeitsch. f. angew. Chem.*, 1923, 404–405.

The following patents of Soc. Ind. et Produits Chimique, Azote Français, Matignon, Rollason and others give further details regarding the production of urea, synthetic ammonia, and so forth (French Patents 527,733, 529,102, 526,188, 530,124 ; Swiss Patent 87,562 ; German Patent 345,256).

English and American Processes of Maxted, de Jahn and Others.—Maxted states that he has produced ammonia at a concentration of 1·23 per cent. at 2,580° C. without the use of pressure (*J. Chem. Soc.*, **113**, 168 (1918)). His assertions are described as impossible by Moldenhauer (*Chem. Ztg.*, 73 (1924)) ; see also *Zeitsch. Kompr. u. flüssiger Gase*, **22**, 1, 29, 41 (1922); *J. Ind. Eng. Chem.*, **14**, 791 (1922).

The American process of de Jahn, which was a complete failure at Sheffield, Ala., is said to work at 80 to 90 atm. pressure and 520° to 550° C. in presence of pumice covered with metallic sodium. The patents of the Nitrogen Corporation, Clancy, and others, describe, *inter alia*, catalysts made from calcium cyanamide or double compounds, such as $K_4CrC_6N_6$, $CaCoC_6N_6$, etc. ; Swiss Patents 94,850, 94,862 ; British Patents 163,046/1921, 143,550/1920, 163,047/1921, 180,314/1922, 140,439/1920, 179,155/1922 ; U.S. Patents 1,399,807, 1,425,577 ; French Patents 517,327, 529,434, 525,504, 532,066, 534,618, 535,104). Other references of general interest are U.S. Patent 1,388,995 ; British Patent 145,060/1921 ; and *J. Ind. Eng. Chem.*, **14**, 611 (1922).

The Italian processes of Casale and of Fauser have so far been dealt with very little in the literature (British Patent 1,488,885/1920, 152,975/1919 ; French Patents 518,355, 534,721 ; U.S. Patents 1,384,428, 1,408,987 ; Swiss Patent 89,819).

CHAPTER XXI

The Cyanide Processes

THE production of cyanogen compounds from atmospheric nitrogen will only be discussed here in so far as it forms an intermediate stage in the production of ammonia and other nitrogenous compounds. Those processes which are essentially concerned with the production of cyanide as their final object need not be discussed here in detail, more particularly as they have already been exhaustively dealt with by F. Muhlert.[1] W. Moldenhauer [2] has published a valuable work on the reactions of free nitrogen and on the historical development of the cyanide syntheses.

Muhlert sub-divides the processes which aim at the production of cyanogen compounds from atmospheric nitrogen as follows :—

(*a*) Hydrocyanic acid from nitrogen, carbon and hydrogen or hydrocarbons.

(*b*) Cyanides from nitrogen, carbon, or carbon compounds and metallic oxides, and finally

(*c*) Calcium cyanamide.

Morren [3] first obtained "synthetic cyanogen compounds" in 1859 ; the product actually obtained by him was hydrocyanic acid, and he obtained it by passing an electric arc between carbon electrodes in an atmosphere of nitrogen. At a much earlier date—namely, in 1828—Desfosses [4] stated that nitrogen was readily absorbed by red-hot wood charcoal soaked in alkali, with formation of alkali cyanide. These two observations formed the basis of a new chemical industry ; a first attempt was made at the time to fix atmospheric nitrogen in a useful form. The demand for cyanide, which could easily be obtained from spent oxide, was very small in the middle of the last century. Activity therefore soon slackened in this direction, although Margueritte and Sourdeval [5] obtained very satisfactory results in 1862. When, however, the cyanide process was introduced in the metallurgy of gold, the cyanide market became active, and interest in synthetic methods was revived. Scheele [6] already knew

[1] F. Muhlert, "Die Industrie der Ammoniak und Cyanverbindungen," Leipzig, 1915.
[2] W. Moldenhauer, "Die Reaktionen des freien Stickstoffs," Berlin, 1920.
[3] *Compt. rend.*, **48**, 342 (1859).
[4] *Ann. de Chim. et Phys.*, **38**, 158.
[5] See the works already cited and also Bertelsmann on Cyanogen Compounds in Ullmann's "Encyclopædia," vol. iii., which includes a bibliography.
[6] K. Nugel, "Gold," in Ullmann's "Encyclopædia," vol. vi. (1919).

in 1782 that gold dissolved in cyanide solutions. This reaction was first patented in Great Britain in 1840 in connection with electroplating. In 1844 Elsner published details of this reaction. In 1867 J. H. Rae first obtained patent protection in the United States for the use of cyanide solutions in the treatment of gold ores. The process employed to-day was then evolved by J. S. MacArthur, R. W. Forrest and W. Forrest in Glasgow in 1886. The first industrial plant was erected in Karangahake, New Zealand, in 1889, the first South African plant at Johannesburg, in 1890, and the process subsequently extended rapidly in America.

In the early 'nineties of last century, Frank, Caro and their associates commenced to study the reactions of calcium carbide with a view to fixing nitrogen technically to form cyanides. Their results were first published in German Patents 88,363 of March 21st, 1895, and 95,660 of January 1st, 1896. For a long time they believed that they had obtained cyanide, until later investigations showed that they had actually obtained a new material, calcium cyanamide (German Patent 108,971 of June 16th, 1898) which we have already discussed as the principal ingredient of nitro-lime. They thus obtained a different result to that which they had anticipated; they had discovered a nitrogen fixation process which was comparatively easy in practice, but they had not discovered the desired cyanide synthesis. On further investigation of the properties of calcium cyanamide, it was found that by melting it with hydroxides or carbonates of the alkalis (German Patents 116,087 and 116,088), or with sodium chloride, it was readily converted into the desired cyanides (German Patent 260,064).

These processes are of no technical importance for the manufacture of cyanide, but they led to a more intensive study than hitherto of the fixation of atmospheric nitrogen with formation of cyanides or cyanogen derivatives. Still, however, no definite success had been achieved in this direction, although Dieffenbach, Moldenhauer, and the Chem. Fabrik. Griesheim-Elektron invented an improved synthesis of hydrocyanic acid [1] which promises to become of technical importance (see German Patents 228,539, 229,057, 255,073, 260,599), but which did not lead to technical co-operation of the cyanide and the nitrogen fixation industries. It is only quite recently that the problem of obtaining ammonia and other nitrogen compounds from atmospheric nitrogen by way of cyanide has been technically solved, as the difficulties to be overcome were greater than was originally assumed. Numerous patents and other publications which may be considered as predecessors of the actual industrial processes of J. E.

[1] Lipinski and Moscicki, *Zeitsch. f. Elektrochem.*, 1912, p. 729.

Bucher and Th. Thorssell are described in the works we have referred to and in the annual reports in the *Chemikerzeitung*. We must refer to them again here.[1] The main object of all this work was, and is, the production of alkali cyanide as such, and not the synthesis of other nitrogen compounds from cyanide formed more or less as an intermediate product.

A paper by John E. Bucher,[2] entitled "The Fixation of Nitrogen," in the *Journal of Industrial and Engineering Chemistry*, March, 1917, pp. 233–253, gives a detailed description of the process described in his lecture at the Ninth Annual Meeting of the American Institute of Chemical Engineers, January 10th to 12th, 1917. I reproduce his introduction herewith :—

"The herein described process for the fixation of nitrogen differs primarily from all those now in commercial use in fixing nitrogen in the form of alkali cyanides instead of in the form of oxides of nitrogen, calcium cyanamide, nitrides, or ammonia. It is further characterised by operating at very moderate temperatures, such as 900° to 950° C., so that it is not dependent upon cheap electric power, and, it can, because of this moderate temperature, be operated in iron retorts. It is of the utmost simplicity, uses iron, which is the cheapest metallic catalyser, and does not require pure materials such as nitrogen, but can use air or producer gas just as well. It requires no special apparatus and can hence be operated at once with what can be found in practically every manufacturing community. It does not require skilled labour to operate it, and it is pre-eminently a method which can be installed quickly in an emergency for the preparation of cyanides, ammonia and nitric acid. These statements are based on a very large amount of chemical and engineering work, most of which was done three to five years ago, and which has appeared only in the form of patents from time to time. I have not heretofore published anything regarding any part of this work. . . . The popular idea seems to be that it is necessary to have cheap hydro-electric power to provide such quantities of nitric acid, together with a costly plant which would require considerable time for its construction. The data already accumulated in my work show that electric power is not necessary, and that the process can be installed in a short time on any scale desired and at comparatively small expense. I had not intended to publish anything on my nitrogen fixation work for a few years more, until I could complete some further important engineering work connected with it. The above

[1] See also *Chem. Ztg.*, 1913, No. 110; 1915, No. 118; 1919, No. 131; 1920, No. 102, p. 839.
[2] *J. Ind. Eng. Chem.*, 11, 946 (1919); *Chem. Zentralbl.*, 1920, iv., 707.

considerations, however, led me to the conclusion that I could not in justice delay action any longer, and hence your kind invitation to present this paper was accepted with the hope of completing the work as opportunity offers."

According to Bucher, the question of the production of cyanide from atmospheric nitrogen was pursued with special activity in the years 1840 to 1847. In 1839 L. Thompson [1] published an experimental investigation in which he showed that it is easy to obtain large quantities of cyanide by the action of air on a mixture of 2 parts of potash, 2 parts of coke, and 1 part of iron filings at a red heat. In this manner he produced 2·8 oz. of Prussian blue from 1 lb. of potassium carbonate. This admirable work was recognised by the Society of Arts by the award of the Golden "Isis" Medal. It was really the foundation of the processes which have now become important, although the results were unquestioned and were the object of scientific discussion between Berzelius,[2] Erdmann and Marchand,[2] Fownes and Young,[2] Langlois,[3] Rieken,[2] Delbrück,[2] Bunsen and Playfair.[2]

In 1840 and 1843 Newton [4] made the first large-scale attempts to operate according to Thompson's proposals. He established a small works at Newcastle-on-Tyne in which he manufactured more than 1 ton daily of potassium ferrocyanide for a long period. The production costs were 1·86 fr. per pound. He passed air through retorts which were charged with wood charcoal soaked in potash, but had to work at a white heat, as he ignored L. Thompson's statements on the catalytic effect of iron. His process failed on account of these high temperatures and the plant difficulties associated therewith, and he ceased manufacture in 1847; but the process is of special interest, as it was the first which was worked on a manufacturing scale.

Between 1881 and 1885 V. Alder, of Vienna,[5] took out patents in which he pointed out the accelerating action of manganese, chromium, nickel and cobalt. These patents contain such a medley of correct and incorrect data that the proposals which they embody have never been translated into practice (German Patents 12,351 and 18,945).

Bucher also refers to Castner's U.S. Patent 577,837 (1897) and Acker's U.S. Patent 1,019,002 (1912), in order to show how completely Thompson's original investigations had been forgotten in the interval.

[1] "Improvement in the Manufacture of Prussian Blue"; *Mechanics Magazine*, No. 822, May 11th, 1839, p. 92; *Dinglers polytechnisches Journal*, New Series, **23**, 281 (1839); W. Moldenhauer, *loc. cit.*, p. 98.
[2] W. Moldenhauer, *loc. cit.*, p. 98.
[3] *Ann. Chim. Phys.* (3), 1, 117.
[4] Bertelsmann, "Die Technologie der Cyanverbindungen," Berlin, 1906, p. 85.
[5] *Ibid.*, pp. 90–91.

We have extracted from Muhlert's book and other sources a short summary of such important patent literature on this subject as cannot be considered in detail here :—

Moermann and Laubuhr	French Patent	108,037.
L. and A. Brin .	German Patent	15,298.
Mond . . .	,, ,,	21,175.
Fogarthy . .	U.S. Patents	598,918, 615,266.
de Lambilly . .	German Patents	63,722, 69,316.
	French Patents	199,977, 202,700, 210,365.
Hunt . . .	British Patent	16,700/1893.
McDonnall . .	,, ,,	772/1894.
Gilmour . .	German Patent	73,816.
Pfleger . . .	,, ,,	88,115.
Aitken and Falkirk	,, ,,	84,078.
Readman	British Patent	6,021/1894.
	French Patent	243,129.
Swan and Kendall . .	British Patent	3,509/1895.
	German Patents	87,780, 244, 496.
Mehner	,, ,,	91,184, 94,493, 151,644, 227,320
Petschow . . .	,, ,,	94,114.
Feld	,, ,,	149,803.
B.A.S.F.	,, ,,	190,955, 197,394, 200,986, 235,662.
Kaiser	French Patents	454,237, 454,238.
Castner . . .	British Patent	12,218/1894.
Moïse	German Patent	91,708.
Schmidt	,, ,,	176,080, 180,118.
Ampère Electrochemical Company		149,594.
Erlwein.		199,973.
Nitrogen Company . .		261,508.
Caro		212,706.
Gros. Grissedet and Others	French Patent	460,684.
Acker	U.S. Patent	1,072,373.
	German Patent	270,662.

Bucher's first investigations were concerned with the formation and the decomposition of magnesium nitride, and led to no important original results.

His attempts to convert alkali metals into cyanide were more important :—

$$2Na + 2C + N_2 = 2NaCN + 46,200 \text{ cal.}$$

Bucher's apparatus consists of a ½-inch tube, 30 inches long, with 1-inch gas inlet and outlet at the ends. This inner reaction tube is surrounded by a wider tube, through which a current of hydrogen or nitrogen is passed in order to prevent carbon dioxide from diffusing into the inner tube from without, and thus forming carbonate with the alkali metal. The whole apparatus is heated in an ordinary combustion furnace. The reaction tube is filled with soot, that is, with perfectly pure carbon free from ash, which is first heated to a white heat in a stream of hydrogen; 40 grams of metallic sodium are then added, and the whole is heated for 25 hours to a red heat in a current of nitrogen. The formation of cyanide is slow. The cooled tube still contains 0·5 gm. of sodium and 23·7 gm. of sodium cyanide, constituting a 79 per cent. yield. When using finely powdered Acheson graphite and 12 gm. of sodium, 58 per cent. of cyanide is formed at a red heat in a current of nitrogen in 20 hours. The charge is now altered, after careful ignition in a stream of nitrogen, by adding a mixture of 120 gm. of finely powdered iron, cleaned with alcohol, 12 gm. of well-ignited lamp black, and 7 gm. of metallic sodium; nitrogen absorption occurs at temperatures below a dull red heat, and so rapidly that a vacuum may be produced in the reaction tube. Argon alone escapes, and 94 per cent. of the sodium is converted into cyanide. The contents of the tube are now free from carbon, and consist essentially of a silvery-white, porous core of iron which is so malleable that it can be beaten out to a flat sheet in a mortar. Globules of molten iron indicate that the internal temperature must have been very high locally. An attempt to convert 4 gm. of sodium mixed with lamp black into cyanide in a copper tube failed; 10 c.c. only of nitrogen were absorbed by the charge, showing that in the first experiment the catalytic action of the iron tube played an important part. The experiments therefore show that iron must be considered as an excellent catalyst, and that the cyanide formation is so strongly exothermic that argon may be prepared in this manner, and that by means of this reaction argon and nitrogen may be quantitatively separated in gas analysis.

Bucher also calls attention to the remarkable fact that the iron used as a catalyst is considerably purified. It loses the whole of its contents of carbon and a large proportion of its phosphorus, sulphur, silicon, manganese and other impurities, and becomes silvery white and soft; in short, it shows all those properties which are associated with electrolytic iron. When one remembers that the electrolytic iron industry has only disappeared in Germany on account of the high cost of current and the complications of the electrolysis, and if one further considers the excellent electrical and mechanical pro-

perties of electrolytic iron, it appears as though pure iron obtained as a by-product of the cyanide synthesis may find useful application. Bucher has succeeded in obtaining compact masses of iron in a silvery-white and soft form by treatment with alkali metals and nitrogen. According to the duration of the treatment the iron is converted into a pure carbon-free modification, either at the surface or throughout the entire mass. Bucher then investigated in detail the reaction :—

$$2NaCN + (\text{pure iron}) = 2Na + N_2 + (\text{iron containing carbide}).$$

For a long time use has been made of the fact that cyanide reacts with iron in the sense of the above equation from left to right in case hardening by means of cyanide or calcium cyanamide. Bucher shows that by heating sodium cyanide with pure iron powder in an iron tube considerable quantities of sodium or potassium can actually be obtained. Molten iron and alkali cyanide react in similar fashion. Hitherto Bucher has not pursued this subject further.

The industrial application of alkali metals for the manufacture of cyanide is neither cheap nor otherwise to be recommended, and Bucher therefore attempts to combine the well-known method of production of alkali metals with the formation of cyanide :—

$$(1)\ Na_2CO_3 + 2C \rightleftharpoons 2Na + 3CO.$$
$$(2)\ 2Na + 2C + N_2 = 2NaCN.$$

The earlier experiments had shown that equation (2) is easily carried out at a red heat if iron is used as a catalyst. Bucher concludes that if even traces of alkali metals are formed according to equation (1) at temperatures of 860° to 980° C., cyanide will be readily produced, as by the law of mass action fresh quantities of alkali metal will immediately be liberated when that already present has reacted according to equation (2). It is of course essential that at the temperatures mentioned, the reaction according to equation (1) should actually take place with sufficient speed.

In a further experiment Bucher verified his conclusions. He heated 10 gm. of finely powdered graphite with 5 gm. of soda for fifty minutes at 920° to 940° C., and was able to show the formation of small quantities of free sodium, whilst when working in a copper tube very little, if any, cyanide is produced in this way. No trace of sodium is formed from 30 gm. of finely divided iron and 5 gm. of soda in a current of nitrogen at 920° to 1,000° C. in 50 minutes. The next decisive experiment, which was already carried out in 1912, was as follows :—[1]

A mixture of 10 gm. of powdered graphite, 10 gm. of finely divided

[1] See Experiment 5, p. 236, of the quoted original publication.

iron, and 5 gm. of soda is heated for 50 minutes in a ½-inch iron tube in a current of nitrogen to 920° to 940° C. Carbon monoxide is formed and 60 per cent. of the contents of the tube are converted into cyanide.

Thompson's statements on the importance of the addition of iron are confirmed, and at the same time it is shown that the reaction can be technically utilised. In Thorpe's "Dictionary of Applied Chemistry," revised edition, vol. ii., p. 196 (1912), Ewan mentions that potassium vapours are not liberated from mixtures of potash and wood charcoal below 1350° C., whilst at this temperature potassium cyanide is formed very slowly. Bucher states that quite satisfactory results can be obtained at 860° to 950° C. with mixtures of iron, soda and charcoal. Bucher confirmed his result by hundreds of experiments. In these he used powdered wood charcoal, coke, lamp black, soda, potash and also the carbonates and hydroxides of cæsium, rubidium and barium. Various horizontal experimental iron tubes were used, some being 6 inches wide and 10 feet long, but those which proved best were 2-inch tubes, 10 feet long. In the reaction product alkali was found in no other form than cyanide, this being therefore of 100 per cent. purity. On evaporating the aqueous extract *in vacuo*, residues are obtained without further treatment, containing 95 per cent. of sodium cyanide.

The process had still to be adapted for practical application. It is by no means easy to treat a powdered material with a gas at such high temperatures. The question of briquetting the charge was therefore soon considered. Bucher first prepared briquettes by heating the mixture of soda, coke and iron until the soda was melted. Very durable briquettes are thus produced at a low pressure, and are so active that the whole of the alkali is converted into cyanide in a current of nitrogen in 10 minutes. In spite of these desirable properties, and the possibility of converting the briquettes so formed directly into cyanide, this method was abandoned, on account of technical difficulties.

Soda crystals, $Na_2CO_3.10H_2O$, commence to lose water of crystallisation above 30° C., with conversion into the monohydrate. At 35° C. this change is complete; the compound $Na_2CO_3.H_2O$ is stable up to 104·75° C. Bucher therefore mixes his charge of calcined soda, carbon, and iron with hot water at as high a temperature as possible, and dries rapidly, so that a temperature interval of about 70° is available for briquetting. As it was found that this method worked excellently in small mixers, Bucher adopted it on a large scale. The charge is converted into a dough in a steam-heated kneading machine, and is then passed, whilst hot, into a small meat-slicing machine,

which is power-driven. This latter comprises a cylindrical screw with a steel disc $3\frac{1}{2}$ inches in diameter, perforated with thirty-seven round holes $\frac{1}{8}$ inch in diameter. The knife of the machine is so adjusted that "briquette strips" about 1 inch long are obtained. The finished briquettes thus consist of small cylinders of $\frac{1}{8}$ inch diameter and 1 inch long. The kneading machines hold 9 gallons, and produce 7,200 lb. of briquettes per twenty-four hours, each charge requiring fifteen minutes. By reducing the treatment of each charge to five minutes, the output can be increased to 21,000 lb. With continuous working the small slicing machine produces 5,000 lb. of briquettes per twenty-four hours, and, with intensive working, almost three times as much. The briquettes so produced must be dried very rapidly, so that they may harden, and that very little, if any, $Na_2CO_3.10H_2O$ may be formed, as the formation of this compound splits the briquettes and causes them to crumble rapidly during storage. Drying is suitably carried out by flue gases or in a baker's oven, or a special drier constructed of masonry and iron may be used. In the laboratory the briquettes may be dried in less than two minutes in the hottest part of a Bunsen flame.

The iron powder used in the briquettes is made from iron filings, boiler scale, magnetite, hæmatite or other substances by grinding in an iron ball-mill with balls of manganese steel. It must be so fine that it passes completely through a 100-mesh sieve. The coke is ground to the same degree of fineness, and then mixed with the powdered iron. The mixture of equal parts of iron and coke must be prepared with special care ; it is therefore necessary to grind the two ingredients together for at least one hour. The calcined soda is then added, and the whole ground for a further five minutes. A very intimate mixture is ensured by the addition of water during briquetting and by the melting of the soda in the furnace. Briquettes prepared in this manner yield a product containing 28 per cent. of sodium cyanide. Iron oxides may be used instead of metallic iron ; they are reduced during the first charge, and become especially active when re-utilised in consequence of very fine sub-division.

If the iron is to form an active catalyst, its surface contact with the nitrogen must be very extended. It is therefore evident that a large excess of soda will be unfavourable, as it prevents contact of the iron with the nitrogen. There must be a definite percentage of soda which is most suitable in practice. The following experiments determine this proportion :—

(1) 2 *parts of iron,* 2 *parts of coke,* 1 *part of calcined soda.* 150 grams of these briquettes were heated to 600° to 1,000° C. in a current of nitrogen in a 1-inch iron tube. The reaction was

vigorous and instantaneous. The cooled and fully treated briquettes contained 13·7 per cent. of sodium cyanide corresponding to an 85 per cent. purity.

(2) *Proportions* 1 *to* 1 *to* 1. 150 grams of these briquettes were treated under the same conditions. Temperature 600° to 1,030° C. The experiment lasted 30 minutes, and the reaction was much slower. The treated briquettes contained 20 per cent. of sodium cyanide, corresponding to a purity of 95 per cent.

(3) *Proportions* 1 *to* 1 *to* 2 (*i.e.*, 50 per cent. soda, as compared with 20 per cent. in experiment (1)). 150 grams of briquettes are heated to 600° to 1,090° C. under the same conditions for one hour, as the reaction is slow. The resultant product contains 14 per cent. of sodium cyanide equivalent to 80 per cent. purity.

Thus the speed of reaction diminishes rapidly with increase in the quantity of soda from 20 per cent. to 35 and 50 per cent. With high soda contents the loss of alkali is greater and the reaction temperature is higher.

If the briquettes do not completely fill the horizontal reaction tube, or if they sinter together during the reaction, which is inevitable if fusion occurs, the nitrogen absorption is not uniform throughout the mass, but occurs in layers. In tubes of ½-inch to 1-inch diameter these phenomena are not so noticeable, as they are in wider tubes. In order to show this effect, Bucher charged 25 lb. of the 2 : 2 : 1 briquettes into a 6-inch iron tube, which was placed horizontally in the furnace, and treated them with nitrogen for 80 minutes at 1,000° to 1,080° C. The charge sank ½ inch during the experiment. A semi-circular channel was thus formed through which the nitrogen was able to pass without obstruction, and in consequence the nitrogen absorption was poor. The average proportion of sodium cyanide was only 3·5 per cent. In the centre of the tube there were a small upper layer containing 12·5 per cent. of sodium cyanide, a thick middle layer containing 3 per cent. of sodium cyanide, and below this, on the floor of the tube, a portion containing only 1·4 per cent. When vertical 6-inch tubes are employed the results are more favourable.

Such a tube was charged with 50 lb. of 1 : 1 : 1 briquettes which were heated in a rapid current of nitrogen to 1,000° to 1,090° C. The experiment lasted for 70 minutes, and a product was obtained which contained 24 per cent. of cyanide above and 20 per cent. below—that is, an average of 22 per cent., equivalent to 10 lb. of cyanide. The carbon monoxide escaping during the reaction burnt in the form of a yellow flame 4 to 5 feet in height.

These experiments, which were followed by many others,

showed that it was necessary to work in vertical retorts on the large scale.

In order to establish the effect of the volatility of the alkali mixture, Bucher repeated these last experiments with 55 lb. of briquettes in a 6-inch tube. The briquettes contained 22 lb. of iron, 24 lb. of coke, and 9 lb. of calcined soda. He heated these for two hours at 1,000° to 1,100° C. After cooling, the upper layer of briquettes contained 28 per cent. of sodium cyanide, corresponding to an 87 per cent. yield. The lower layers contained decreasing percentages of sodium cyanide as follows: 16, 14, 12 and 10 per cent., corresponding to 90 to 93 per cent. purity. The lowest layer consisted in the centre of fairly solid, 12 per cent. briquettes (100 per cent. purity) which were surrounded by a ring of briquettes containing only 7 per cent. of sodium cyanide, which had crumbled to a fine powder. The fact that in the lowest portion all the alkali was present as cyanide (hence the 100 per cent. " purity ") showed that the heat and the rapid current of nitrogen had caused a large part of the alkali to volatilise. The uppermost layers are correspondingly rich in alkali, hence the " purity " of 87 per cent. only.

Two means can be adopted of overcoming these difficulties. Either the briquettes must be made so active that they can be converted into cyanide at such low temperatures that the volatility of the alkali is negligible, or a continuous furnace must be constructed in which the volatility may even be of advantage.

In order to study the reactivity of the briquettes, some very interesting and valuable experiments were made, each with 25 gm. of briquettes in a ½-inch iron tube placed horizontally in the furnace. Firstly briquettes containing iron, coke and sodium carbonate in the proportions of 2 : 2 : 1 were heated for 13 minutes at 710° to 920° C. The liberated current of carbon monoxide, which was very rapid at first, vanished after 6 minutes, before the temperature had attained 900° C. The final product contains 15·2 per cent. of NaCN of 92 per cent. purity. This result shows definitely that 2 : 2 : 1 briquettes can be converted within 10 minutes at a temperature below 920° C. into a product containing 15 per cent. of cyanide of over 90 per cent. purity. The briquettes were extracted with water and calcined soda added to the wet filter cake of iron and coke in such quantity that the proportions 1 : 1 : 1 were obtained. On heating to 620° to 920° C. the new briquettes no longer gave rise to violent evolution of carbon monoxide, but the evolution of gas lasted throughout the whole experiment, namely for 28 minutes. The product which was obtained contained 30 per cent. of sodium cyanide of 87 per cent. purity. Products containing 11·5 per cent.

sodium cyanide of 61 per cent. purity were obtained from 2 : 2 : 1 briquettes even at temperatures between 560° and 920° C. Copper tubes, which are not readily oxidised, can be used without special precautions. It is important to note that the extracted briquettes can be remixed with fresh soda in the kneading machine. The new briquettes are used in the same manner as before.

Bucher then considered the construction of the furnace in detail. Continuous cyanisation offers many advantages. Loss of alkali is entirely avoided, as the alkali which evaporates in the hottest portion is condensed and retained by the charge in the colder portion. The first experiment was made in an 8-inch iron tube, 8 feet long, which was placed vertically in a furnace and was connected by means of a T-tube with a screw conveyor immediately below. At first cyanisation proceeded perfectly, but as the hot briquettes entered the conveyor and hardened there, this failed entirely. The following arrangement gave better results: A cast-iron tube 15 feet long (see U.S. Patent 1,120,682) is placed vertically in a furnace in such a manner that below the actual reaction space, which is heated by an oil burner, there is a cooling chamber about 4 feet long (Fig. 18). The white-hot plastic briquettes from the reaction zone are here cooled by the injected current of cold nitrogen and by the outer air. The cooling effect can be intensified by passing water into the outer chamber or by applying moist cloths. The briquettes become cold and hard, and pass through the discharging screw conveyor without difficulty. They then enter a cooling and storing chamber from which they can be removed as required. In their external character the cyanised briquettes issuing from this furnace are similar to those with which it is charged by the upper screw conveyor. As, however, the briquettes often jam in the tube, a claim is made in U.S. Patent 1,120,682, for constructing the whole reaction tube or its lower portion in conical form. The difficulty may also be overcome by using larger and heavier briquettes, or by adding briquettes

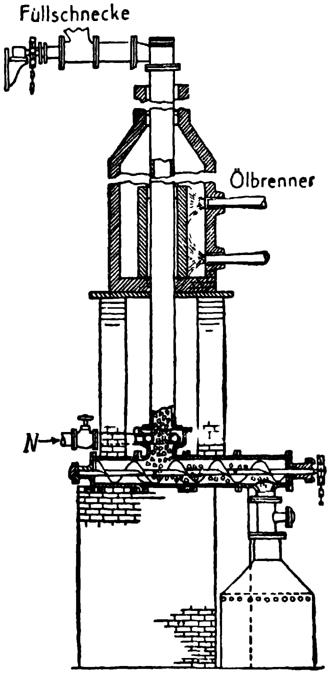

FIG. 18.
Füllschnecke = Charging screw conveyor
Ölbrenner = Oil burner.

containing less alkali, or lumps of coke, at the outer circumference, the inner portion being reserved for the normal briquettes. The simple plan may be adopted of constructing the cooled portion of wider tubing as shown in Fig. 19.

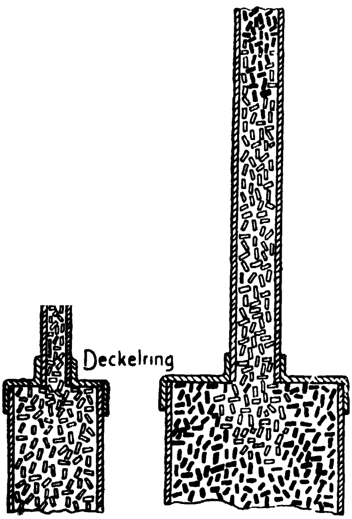

FIG. 19.
Deckelring=Circular cover.

Bucher claims to have solved this difficulty completely by constructing the cooling zone of such width that the hot briquettes from the furnace, which are shown white in Fig. 19, are completely cooled before coming into contact with the walls. In this case the cooled (black) briquettes protect the walls. Bucher found that it was only the briquettes which had already become hard which stuck to the wall, whilst the hot briquettes always pass down the furnace tube easily and without hindrance. Obstructions occasionally occur at the upper end of the actual reaction chamber, but can be avoided by certain precautions.

An iron tube, 22 feet long and 8 inches wide, holds 500 lb. of briquettes during experiment, and has an output capacity of 3,000 lb. per twenty-four hours.

At a later date the furnace was improved in many respects. It now consists of a double chimney with a thin partition between the two divisions. The flame of an oil burner, or preferably of a gas burner, burns in the first division from above downwards, and then passes through flues into the second division, in which the 22-feet tube is contained and is surrounded by the flame. By controlling the draught at the upper end, the temperature of the furnace is controlled and an even temperature is maintained by blowing in air through slits into the flame. The whole furnace is so arranged that the reaction tube can readily be removed and replaced by means of a crane when necessary.

In his article Bucher also describes the electric furnaces constructed and used by him, which consist in their simplest form of a piece of $1\frac{1}{2}$-inch galvanised iron tube which is provided with electric terminals insulated by thick layers of magnesia-asbestos and placed in a shaft of masonry. Briquettes containing 22 per cent. of NaCN have been produced in such furnaces. We must refer for details to the original publication, which gives exact data and from which the most

important details can be gathered. He describes, for instance, an interesting form of furnace, which is charged with molten iron and coke, through which sodium vapour and nitrogen are injected. A steady current of sodium cyanide vapour is thus obtained, together with carbon monoxide.

With the purpose of investigating the process in every detail, Bucher has made temperature measurements in his furnace. He charges a 4-inch iron tube with 8 lb. of the 2 : 2 : 1 mixture of iron, coke and soda, in briquette form, and places a pyrometer in the middle of the shaft. The furnace is heated by an oil burner, the flame temperature of which is measured with a pyrometer. The following table shows the extraordinary differences in the readings at any one time :—

	Without.		Within.
Initially . . .	+ 1,030° C.	..	+ 150° C.
After 40 minutes .	+ 1,080° C.	..	+ 800° C.
After 60 minutes .	+ 1,080° C.	..	+ 1,010° C.

Thus the transference of heat is very slow, as is natural when one considers that 138,500 cals. have to be absorbed in order to carry out the reaction. A final product was obtained containing 17 per cent. of sodium cyanide of 99 per cent. purity. The experiments showed that the uniform heating of a column of briquettes 6 or 8 inches wide requires a considerable period, so that pre-heating is always advisable.

It is naturally advantageous to heat the mixture electrically by internal resistance. In furnaces constructed on this principle, Bucher states that he has cyanised small quantities within one minute, and several pounds within a few minutes.

In order to determine whether pure nitrogen is necessary for cyanisation, Bucher carried out a number of experiments with air, which he first passed over hot coke. He carries out his experiment by filling the front portion of a horizontal reaction tube with lumps of coke, behind which he places a porous diaphragm and then fills the end portion of the tube with briquettes in the usual manner. The tube is heated to a high temperature in the furnace, and air is blown through, first passing the red-hot coke and then the briquettes. Cyanisation was just as good as when pure nitrogen was used, but of course there was a larger evolution of carbon monoxide. Lighting gas, flue gases and so forth may be used instead of air. An interesting duplicate experiment was carried out in which a 6-inch and a 4-inch iron tube were heated together in the same furnace. Both tubes were placed vertically, were closed at the lower end and filled with a layer of coke, about 1 foot in height, above which there was a 72-lb. charge in the form of briquettes. Through each tube nitrogen was

passed on one occasion and air on the other. The result was that the resulting mass contained 19 per cent. of sodium cyanide when air was used and 18 per cent. when nitrogen was used, that is to say, the degree of cyanisation was practically constant.

Nitrogen was readily obtained for the experiments by passing air over copper in the usual manner, periodically reducing the copper oxide which was formed. It is also possible to burn hydrogen in air in iron tubes with a fireproof lining and to condense the steam which is formed.

When extracting the cyanised briquettes it is not advisable to leach them and then evaporate the solution. The method of removing the cyanide by distillation appears to be much more suitable. Temperatures below 1,120° C. must be used, as otherwise the iron melts partially with destruction of the catalytically active surface. The attainment of this critical temperature is avoided by the use of a vacuum. From briquettes contained in a closed copper tube the sodium cyanide may be quantitatively removed as a clear melt by distillation at 1,000° C. and at 2 mm. pressure. The residue contains traces only of alkali. The distilled cyanide is of 99 per cent. purity. By including a small tube filled with sodium chloride, Bucher showed that the distillation of sodium cyanide or potassium cyanide *in vacuo* must occur at temperatures below 792° to 820° C. Potassium ferricyanide, $K_3Fe(CN)_6$, and potassium ferrocyanide, $K_4Fe(CN)_6$, yield on distillation *in vacuo* pure potassium cyanide, together with a residue of very finely divided iron and carbon, both of which may advantageously be used for cyanisation.

If the residues remaining on distilling the cyanide are repeatedly used for briquettes and thus reintroduced into the cycle, with addition of new quantities of soda and coke, the proportion of ash from the latter necessarily accumulates until it finally prevents the reaction from occurring. Ash-free carbon, which would, of course, be the most suitable for the purpose, can be obtained, for example, according to the following equation :—

$$2CO \rightleftharpoons C + CO_2 + 38{,}080 \text{ cals.},$$

the equilibrium of which is almost completely in the direction of the formation of carbon monoxide at 1,050° C., and in that of the formation of carbon dioxide at 500° C. Bucher attempted to convert carbon monoxide into pure carbon and carbon dioxide with the help of catalysts. On passing carbon monoxide over powdered heated coke, scarcely any carbon dioxide is obtained. If, however, carbon monoxide is passed over heated, finely divided iron in a combustion tube, it is at once decomposed into free carbon and carbon dioxide,

of which the escaping gaseous mixture contains 40 per cent. The idea of combining this reaction with the cyanising reaction is promising. In this manner it should be possible to produce finely divided carbon at the iron surfaces of the iron and soda briquettes. The later experiments of Bucher were directed to this object.

Mond [1] found that 15 parts of nickel caused the deposition of 85 parts of carbon. Bucher, on the other hand, never obtained higher concentrations of carbon dioxide than 43 to 45 per cent., and suggests that at this point an equilibrium condition is attained in presence of iron. He confirms this view by reference to the literature, according to which, in the presence of CO_2, CO, Fe and C, a definite equilibrium is attained at which carbon dioxide commences to oxidise iron to ferrous oxide. In the presence of metallic iron, equilibrium is attained when about 42 per cent. of CO_2 and 58 per cent. of CO are present at about 680° C. Nickel is not so readily oxidised as iron. It is therefore possible to decompose carbon monoxide almost quantitatively into carbon and carbon dioxide by passing it over nickel at 300° to 400° C., carbon dioxide of 98 per cent. purity being thus obtained. No difficulty through oxidation of the iron tube of the cyanising apparatus appears to occur. At 150° C. the presence of 25 per cent. of CO_2 appears to be sufficient to prevent such oxidation, and, moreover, the nitrogen and the combustion gases which diffuse through the wall of the tube appear to exert a protective action. Copper and nickel are equally durable.

The catalytic activity of iron is explained by Bucher on the assumption that the carbon dissolved in the iron plays the main part.

The average purity of the evolved carbon monoxide is 75 per cent. In the laboratory the whole of the nitrogen may be quantitatively absorbed, and the gases which finally escape contain 100 per cent. of CO.

The behaviour of producer gas, which may be used instead of nitrogen, is quite exceptional. In an experiment carried out at a red heat, the cyanised briquettes contained 19 per cent. of sodium cyanide ; if they were then allowed to cool in the gas current, they contained 3 per cent. of sodium cyanide only after cooling, showing that an energetic and rapid reversal of the reaction had occurred. If the current of producer gas is cut off and the cyanised briquettes allowed to cool in air, nitrogen or any other inert gas, the reversal of the reaction does not take place, and the contents of sodium cyanide remain unaltered. Bucher attributes this remarkable behaviour to the action of carbon dioxide, which is produced from the iron and

[1] *Journ. Amer. Chem. Soc.*, **57**, 749 (1890).

carbon monoxide. As the concentration of the CO_2 is especially high at 600° to 700° C., the decomposition of the cyanide in the briquette is most intensive at these temperatures. At temperatures between 950° and 1,000° C. scarcely any carbon dioxide is produced, and the decomposition of the cyanide does not occur.

In the continuous furnace the untreated briquettes first pass through a preheating zone, in which they are heated by the reaction gases from the furnace. Vapours of alkali and of cyanide from the hotter portions of the furnace condense on the cool surfaces of these briquettes. The briquettes gradually become red-hot. The carbon monoxide evolved from the cyanisation zone commences to be decomposed at the iron contact,

$$2CO = C + CO_2 + 38{,}080 \text{ cals.},$$

with formation of exceedingly active carbon, whilst a considerable quantity of heat is evolved which is of great importance for the cyanisation, as this absorbs considerable quantities of heat :—

$$Na_2CO_3 + 4C + N_2 = 2NaCN + 3CO - 138{,}500 \text{ cals.}$$

The lower portion of the furnace serves to preheat the nitrogen and simultaneously to cool the finished briquettes. The carbon dioxide in producer gas may be removed by washing with a solution of caustic alkali ; under such circumstances other factors require consideration. In an iron tube 14 feet long and 6 inches wide only 5 per cent. of cyanide instead of the expected 20 per cent. is obtained if 2,000 lb. of briquettes are treated, or only 1 per cent. if 1,000 lb. of briquettes are passed through it daily ; the decomposition is therefore very considerable.

These considerations are of great importance in designing a continuous furnace fed with producer gas. It has been found that all difficulties are overcome if the producer gas is introduced at the foot of the hottest zone. Carbon dioxide is unstable under the conditions occurring in this zone, and is converted into carbon monoxide. The briquettes cool as they descend and are immediately removed from the injurious action of the producer gas. The lower part of the tube furnace must be absolutely gas-tight, as otherwise the gases may pursue a wrong path. The appended diagram (Fig. 20) shows a section of a furnace which may be supplied either with producer gas with the help of a compressor or with pure nitrogen. In either case briquettes are obtained containing 25 per cent. of sodium cyanide.

In the Bucher process the speed of reaction is limited both by the activity of the briquette and by the rate at which nitrogen and heat penetrate throughout the charge. The briquettes themselves

react in 1 to 2 minutes, and the necessary nitrogen passes, for example, through a tube 6 feet long and 6 inches in diameter within 10 minutes. On the other hand, about 2 hours are required for heating. From these data it is clear what a very great influence an improved method of heating would have on the economics of this process. Heating by internal electrical resistance and the utilisation of the carbon monoxide decomposition, according to the equation,

$$2CO = C + CO_2 + 38{,}080 \text{ cals.},$$

are therefore very desirable. The greater the length of the heating zone the more economically does the furnace work. In order to promote downward movement of the briquettes the tube may be mounted at a slight inclination.

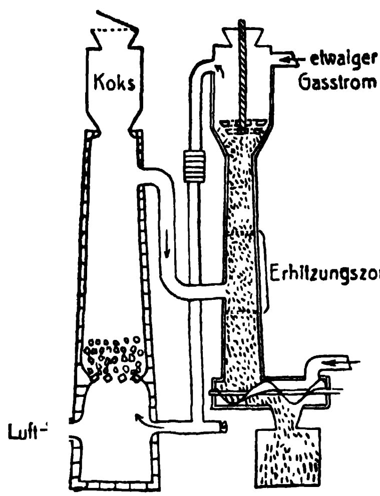

FIG. 20.
Koks = Coke.
Luft = Air.
Etwaiger Gasstrom = Gas inlet.
Erhitzungszone = Heating zone.

Two methods have been mentioned for further treatment of the cyanised briquettes, namely, simple leaching and distillation *in vacuo*. When leaching is resorted to certain precautions must be observed in order to obtain the desired results. If the cyanised briquettes are treated with a little hot water and the whole then heated with steam in a vessel provided with a stirrer, the following reaction occurs :—

$$6NaCN + Fe + 2H_2O = Na_4Fe(CN)_6 + 2NaOH + H_2,$$

resulting in the complete conversion of the sodium cyanide into sodium ferrocyanide and caustic soda, with evolution of large quantities of hydrogen. After heating for several hours the hot mass may be filtered, and the residue of iron and powdered coke is returned into the cycle of processes.

From the hot filtrate sodium ferrocyanide separates on cooling ; on concentrating further the remainder is separated and a concentrated solution of caustic soda remains, which may be carbonated and returned to the process or treated in any other manner.

Sodium cyanide crystallises as $NaCN.2H_2O$ at temperatures below 35° C., whilst above that temperature it remains in solution as the anhydrous salt. Therefore if the cyanised briquettes are extracted with water at a temperature just over 35° C., and the

solution, immediately filtered from the residue, a pure solution of sodium cyanide is obtained, as the formation of sodium ferrocyanide is a much slower process and requires higher temperatures. The solution is evaporated *in vacuo* and yields a cyanide which is sufficiently pure for most purposes. It may be further purified by distillation *in vacuo*. In order to decompose any soda, lime is added; both NaOH and Na_2CO_3 tend to prevent the dissociation which otherwise occurs in aqueous solutions according to the equation:—

$$NaCN + H_2O \rightleftarrows NaOH + HCN.$$

On adding calcium chloride, sodium chloride is formed according to the equation,

$$Na_2CO_3 + CaCl_2 = CaCO_3 + 2NaCl,$$

and on evaporation yields a marketable mixture with the cyanide.

The reactions of sodium cyanide are very interesting and of technical importance. On boiling the solution, for example, the following reaction occurs:—

$$NaCN + 2H_2O = H.COONa + NH_3.$$

At the boiling point of the solution, however, only a very small portion of the cyanide reacts according to this equation, the evolution of hydrocyanic acid predominating. If, however, caustic soda is added, or is produced by the addition of quicklime to the solution, the boiling point is raised and dissociation avoided, and rapid formation of sodium formate occurs, which is salted out by the free alkali, as its solubility in alkaline solution is very much less. These operations may conveniently be carried out under a reflux condenser. After drying with caustic soda, the ammonia which is evolved is perfectly pure. The sodium formate may be returned to the process. It may also be converted into the oxalate by heating *in vacuo*. The corresponding acids are readily prepared from the formate and oxalate.

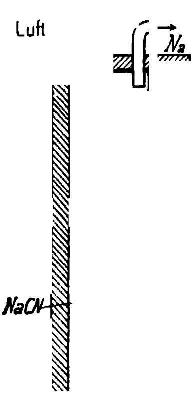

FIG. 21.—Bucher's apparatus for the production of urea from cyanide.
Luft = Air.

A cast-iron vessel 3 inches in diameter and 12 inches deep, with a tight-fitting cover (Fig. 21), is provided with gas inlet and outlet tubes, the former ending in two 2-inch branches. Sodium cyanide is heated in this vessel to a point just above its melting point, whilst a rapid current of air is blown through it. Sodium cyanate is readily produced, and nitrogen escapes:—

$$NaCN + O + 2N_2 = NaCNO + 2N_2.$$

The nitrogen may be returned to the cyanide furnace. Four times as much nitrogen is thus produced as is required for the production of the same quantity of cyanide, so that an excess is provided. On heating with water, the cyanate is decomposed much below the boiling point of the solution, forming sodium bicarbonate and ammonia :—

$$NaCNO + 2H_2O = NaHCO_3 + NH_3.$$

The bicarbonate is returned to the process, and the ammonia may be caused to interact with a further molecule of sodium cyanate to form urea :—

$$NaCNO + NH_3 + H_2O + CO_2 = NaHCO_3 + NH_4CNO ;$$
$$NH_4CNO = CO(NH_2)_2.$$

The necessary carbon dioxide is supplied by the cyanisation process. The reactions are similar to those of the ammonia soda process, which are :—

$$NaCl + NH_3 + H_2O + CO_2 = NaHCO_3 + NH_4Cl,$$

the chlorine atom being replaced by the radical CNO. The urea-producing reaction is not reversible and therefore takes place much more readily than the formation of soda in the ammonia soda process. Bucher recommends urea as a highly active fertiliser, very rich in nitrogen, the use of which does not necessitate the introduction of sulphuric acid into the soil. Field experiments gave very favourable results and showed that the nitrogen in urea was as active as that of potassium nitrate. Urea nitrate $CO(NH_2)_2.HNO_3$ is less soluble in water.

Molten sodium cyanide is readily decomposed by the electric current into sodium and cyanogen. As the melting point of sodium cyanide is lower than that of sodium chloride and its decomposition voltage is also lower, Bucher points out that it presents various advantages over molten sodium chloride as a source of metallic sodium.

Free cyanogen gas is very reactive. It is readily absorbed by 44 per cent. hydrochloric acid, which converts it into oxamide :—

$$(CN)_2 + 2H_2O = C_2O_2(NH_2)_2.$$

During this reaction the hydrochloric acid becomes so concentrated that the acid is partially evolved in gaseous form, whilst the oxamide separates as a heavy white powder. If the concentration of the hydrochloric acid is appreciably lower than 44 per cent. the reaction no longer occurs.

Oxamide contains almost 32 per cent. of nitrogen and is almost insoluble in water. According to trials carried out by Hartwell at

the Rhode Island Experimental Station it is a very valuable fertiliser. In fertilising effect it resembles blood meal rather than nitrate, which is more rapid but less durable in its action.

If oxamide is heated with concentrated hydrochloric acid for one minute, it is immediately converted into oxalic acid which crystallises out in a perfectly pure condition,

$$C_2O_2(NH_2)_2 + 4H_2O + 2HCl = (COOH)_2.2H_2O + 2NH_4Cl,$$

with simultaneous production of ammonium chloride. On heating with glycerine, oxalic acid is rapidly converted into formic acid :—

$$(COOH)_2 = H.COOH + CO_2.$$

To summarise, the most important features of the application of the Bucher process are as follows :—

(1) No action occurs in the absence of iron.

(2) The constituents of the briquettes must be thoroughly well mixed.

(3) The briquettes must not be heated to too high a temperature, as otherwise the iron melts and the active catalyst surface is destroyed.

(4) The retorts must always be placed vertically in the furnace.

(5) The cyanised briquettes must not be cooled in a stream of producer gas.

(6) Presence of oxygen in the gases is very disadvantageous.

(7) It is necessary to maintain a long heating zone in order that the heating may be as uniform as possible and that the briquettes may be heated throughout.

The process is readily carried out on an experimental manufacturing scale, and an electric cyanisation furnace can be erected in a few hours of such size that it produces 150 lb. of sodium cyanide, or more than 200 lb. of sodium ferrocyanide per twenty-four hours. The simplest method of producing the briquettes has already been described. At the time when the details were published, in January, 1917, from the Brown University, Providence, Rhode Island, the ruling prices were \$2·00 per pound of sodium cyanide and \$1·25 per pound of sodium ferrocyanide, and at such prices the cost of the furnace, which is about \$100, is soon recovered.

The reaction,

$$Na_2CO_3 + 4C + N_2 = 2NaCN + 3CO - 138{,}500 \text{ cals.},$$

theoretically requires 35,000 h.p. for the production of 180,000 tons of nitric acid, assuming that the ammonia oxidation gives an 85 per cent. yield of that product. The three molecules of carbon monoxide which are produced supply on combustion, according to the following equation,

$$3CO + 3O = 3CO_2 + 200{,}000 \text{ cals.},$$

50,000 h.p., so that the combined process would actually be exothermic and require no electric power :—

$$Na_2CO_3 + 4C + 3O + N_2 = 2NaCN + 3CO_2 + 61{,}500 \text{ cals.}$$

Compared with the results of the arc and cyanamide processes, these facts promise useful economic results. The cyanide process offers the advantages over the Haber-Bosch process of simplicity and cheapness of the plant. The products which may be produced are very varied.

The very full publication of Bucher may be considered as the most complete exposition of the technical production of cyanides from atmospheric nitrogen and their conversion into other more important substances.

The second important publication was that of Th. Thorssell,[1] at a considerably later date, namely in a lecture on April 20th, 1920, to the Chemical Section of the Technical Society of Gotenburg. The following dates may be quoted from Thorssell's historical table :—

1835. Dawes discovers the occurrence of potassium cyanide in the blast furnace.

1839. Thompson finds that he can absorb nitrogen by mixtures of alkali carbonate, carbon and iron with formation of cyanide.

1843. Possoz and Poissière produce cyanide from alkali carbonate and carbon in a continuous shaft furnace.

1847. Bunsen carries out detailed investigations on nitrogen fixation by mixtures of alkali carbonate and carbon.

1862. Margueritte and Sourderal utilise barium oxide as a base.

1880. Alder protects by patents the manufacture of cyanide from nitrogen, alkali carbonate, carbon and iron.

1882. Mond cyanises briquettes of barium carbonate and charcoal in a ring furnace.

1890. Breneman reports on the attempted syntheses of cyanide carried out up to that date.

1895. Frank and Caro suggest the fixation of nitrogen by a mixture of barium carbide and KOH.

1898–99. Mehner, Rothe, Freudenberg, Frank and Caro explain the nature of nitrogen fixation by calcium carbide.

1899. Täuber rediscovers the importance of finely divided iron in the synthesis of cyanide from alkali, carbon and nitrogen.

About 1910. Th. Thorssell commences his investigations.

1912. Large-scale experiments by the newly formed A.B. Kväfveindustri at Bohus, near Göteborg.

[1] *Zeitsch. f. angew. Chem.*, 1920, i., 239, 245, 251.

1914. Commencement of large-scale technical manufacture which was very soon interrupted by difficulties in the supply of raw materials and by a fire at the works.

1911–12. First experiments by J. E. Bucher.

1912. First patents of the Nitrogen Products Company, Providence, Rhode Island, according to Bucher's process.

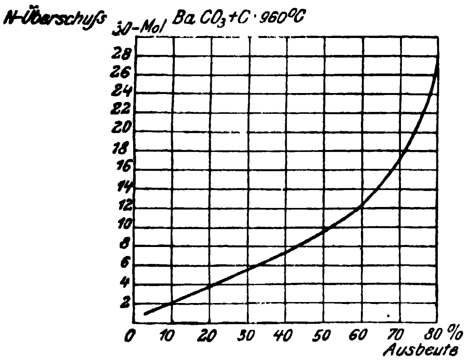

FIG. 22.

Überschuss = Excess. Ausbeute = Yield.

Thorssell considers that the main difficulties of the cyanide process are associated with the application of the heat, which may be carried out by external heating in either continuous or discontinuous retorts or by the use of the ring furnace or by electric resistance heating and so forth. Mehners carried out experiments in 1899 with a 500-h.p. furnace in which the furnace walls themselves act as conductors for the current.

Thompson recommends iron alone as catalyst, whilst Alder (1880) also recommends manganese and nickel. In order to ensure penetration of the reaction mass by the nitrogen, Mond recommended in 1860 that it should be briquetted or granulated.

The reaction velocity of the cyanisation diminishes proportionally to the percentage of carbon monoxide in the reaction chamber and to the increase in the quantity of cyanide; it is also dependent on the temperature of the furnace. High percentages of carbon monoxide are especially unfavourable. They are most easily avoided by working with a considerable excess of nitrogen. The accompanying curves (Figs. 22–24) were obtained when cyanising a mixture of barium carbonate and charcoal, and show the influence of carbon monoxide and of an excess of nitrogen. The reaction occurs according to the equation :—

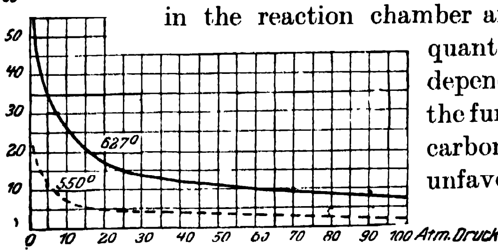

FIG. 23.

Gehalt an CO = Percentage of CO.
Atm. Druck = Atmospheres pressure.

$$BaCO_3 + 4C + 2N = Ba(CN)_2 + 3CO.$$

The reaction velocity decreases as the proportion of cyanide to unchanged carbonate increases. In order to avoid excessive diminution of the reaction velocity by the combined influence of a high concentration carbon monoxide and a large proportion of cyanide, it is necessary to work under such conditions that when the cyanide contents attain a maximum the partial pressure of the nitrogen is also at a maximum. These conditions are necessarily fulfilled in continuously charged retorts or furnaces supplied with a counter current of nitrogen.

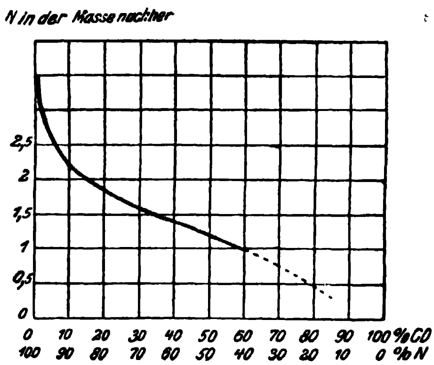

FIG. 24.

N in der Masse nachher = N in final product.

The next curve (Fig. 25)[1] shows the relation between reaction velocity and temperature; the reaction velocity increases with increasing temperature; it is also directly proportional to the pressure.

The reaction mass must be finely powdered, but, according to Thorssell, it is not necessary to add iron as a catalyst when working with barium carbonate and carbon, as in this case iron exerts no influence. Metallic barium is not formed as an intermediate product from barium carbonate and carbon during the cyanisation process, whereas in the case of sodium carbonate and carbon metallic sodium is formed This metallic sodium is supposed to form an alloy with iron, and, as iron also combines with carbon, the conditions are present for intimate contact and therefore for interaction. In the presence of iron the reaction velocity is about as great at 930° C. as it is without iron at 1,000° to 1,100° C. Sodium carbonate is therefore only effective when iron

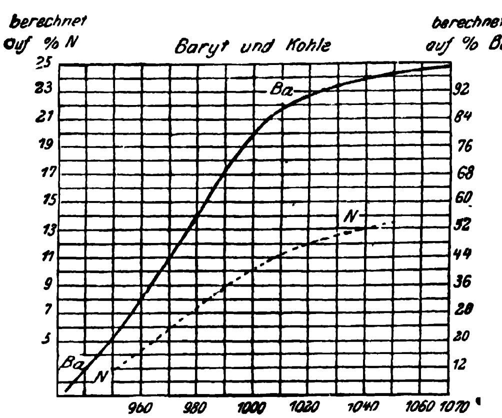

FIG. 25.

Kohle = Carbon. berechnet auf = Calculated on.

[1] *Zeitsch. f. angew. Chem.*, 1920, i., 240.

is also present, as at 1,000° C. the temperatures of formation and of volatilisation of sodium cyanide lie far too close together.

Coke ash always contains silica, alumina, lime, magnesia, potash and soda. Of these potash and soda are entirely unprejudicial to the cyanisation process. On the other hand, silica and alumina form silicates with the alkali or alkaline earth oxides of the reaction mixture, and also with lime and magnesia. These injurious impurities will inevitably accumulate if the residues are permanently returned to the process. Thorssell insists on the importance of this consideration, and advises that a solution of the difficulty should be attempted. Bucher's work gives much more valuable information on this point. The nitrogen should also be as pure as possible.

As it is essential to work with a considerable excess of nitrogen in order to maintain a low concentration of carbon monoxide, this gas must be available at a cheap rate. The method of production by means of metallic copper is far too troublesome, and, according to Thorssell, production by rectification of liquid air, which cost 2 to 5 pfg. per cu. m. before the War, and therefore 20 to 50 pfg. per kilogram of nitrogen, if one allows for a ten-fold excess, is also too expensive. A method was therefore evolved at Gotenburg of obtaining nitrogen by removing oxygen from air by spongy iron at a high temperature. It was found that removal of the oxygen was only practically possible by briquetting powdered spongy iron with soda as a binder. The resultant mixture with iron oxide is once more reduced with water-gas, and a complete cycle of operations is thus achieved. Starting from atmospheric air 0·24 kg. of coke are used per kilogram of nitrogen, and when using flue gases containing, for example, 5 per cent. of oxygen only, 0·05 kg. of coke are required per kilogram of nitrogen which is produced.

The flue gases from the cyanising furnaces always contain carbon dioxide together with the monoxide. Thorssell shows the composition of the flue gases in the accompanying curve (Fig. 26).[1] The continuous lines show the percentages of carbon monoxide and carbon dioxide in the case of a mixture of soda and carbon heated to 930° C., whilst the dotted lines show the results with the same mixture at a temperature below 850° C. The former curves show

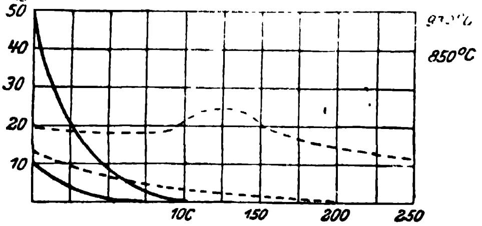

FIG. 26.

[1] *Zeitsch. f. angew. Chem.*, 1920, i., 247.

the rapidity with which the reaction starts and with which it declines, and the others show a more gradual reaction.

In large continuous furnaces during practical working the average proportion of carbon dioxide to the monoxide is 1 to 3.

When the cyanising process is carried out as part of a cycle of operations, the carbonate is returned into the cycle admixed with hydroxide and formate, produced by secondary interaction with the cyanide, which is first formed, with water, producing ammonia. If barium carbonate is used as the raw material, the reaction proceeds smoothly with formation of a basic cyanide, $BaO.Ba(CN)_2$, whilst the normal cyanide, the production of which is unnecessary in practice, is formed much more slowly.

Thorssell gives the following summary of the individual phases of the cyanisation of mixtures of barium carbonate and carbon in a cyclic system of processes :—

Extent to which reaction proceeds.	Reaction.
42 per cent.	$10Ba(HCO_2)_2 + 18C + 10N = 5BaO.Ba(CN)_2 + 7CO_2 + 21CO_2 + 10H_2$ (absorbing 442 cals.).
3 ,,	$10Ba(HCO_2)_2 + 4C = 10BaO + 10H_2 + 6CO_2 + 18CO$ (absorbing 24 cals.).
13 ,,	$10BaCO_3 + 20C + 10N = 5BaO.Ba(CN)_2 + 5CO_2 + 15Co$ (absorbing 130 cals.).
2 ,,	$10BaCO_3 + 6C = 10BaO + 4CO_2 + 12CO$ (absorbing 15 cals.).
35 ,,	$10Ba(OH)_2 + 22C + 10N = 5BaO.Ba(CN)_2 + 3CO_2 + 9CO + 10H_2$ (absorbing 251 cals.).
5 ,,	$10Ba(OH)_2 + 8C - 10BaO + 2CO_2 + 6CO$ (absorbing 25 cals.).

In all 887 cals. are absorbed per 137·4 gm. of barium or per 126 gm. of fixed nitrogen, so that theoretically the reaction absorbs 7,040 cals. per kilogram of fixed nitrogen or 8·2 k.w.h., corresponding to 1·76 kg. of coal. The escaping flue gases contain 840 + 54 + 133 + 16 + 406 + 50 = 1,499 cals., or a heating value of 11,900 cals. per kilogram of nitrogen.

The furnace temperature is so low that it is quite easy to use the flue gases completely for steam-raising, drying, or other purposes. Even though only 60 per cent. of the energy of these gases is effectively utilised, this suffices for the cyanisation. In other words, the heat which is necessary in order to carry out the reaction is recovered in such a form and quantity that the heat requirements of the whole process can be covered.

In the treatment of the cyanised briquettes produced from *soda*

coke and iron, it is important to note that under certain conditions sodium ferrocyanide is produced during the extraction with water. This product may react further with water according to the equation,

$$Na_4Fe(CN)_6 + 11H_2O = 6NH_3 + 4Na.OOC.H + FeO + 2CO,$$

with production of ferrous oxide, which has to be reduced in the furnace at the cost of carbon and energy before it can be re-utilised for nitrogen fixation in the form of metallic iron. The amount of the ferrous oxide so produced is, however, quite unimportant. On the assumption that the yield on cyanisation is 80 per cent., the following summary of the soda-coke-iron process may be presented :—

Degree to which the reaction occurs	Reaction.
73 per cent.	$10NaHCO_2 + 16C + 10N = 10NaCN + 5H_2 + 4CO_2 + 12CO$ (absorbing 453 cals.).
7 ,,	$10NaHCO_2 + 2C = 5Na_2O + 5H_2 + 3CO_2 + 9CO$ (absorbing 37 cals.).
3 ,,	$5Na_2CO_3 + 17C + 10N = 10NaCN + 9CO + 3CO_2$ (absorbing 17 cals.).
7 ,,	$5Na_2CO_3 + 3C = 5Na_2O + 2CO_2 + 6CO$ (absorbing 35 cals.).
4 ,,	$10NaOH + 18C + 10N = 10NaCN + 2CO_2 + 6CO + 5H_2$ (absorbing 17 cals.).
6 ,,	$10NaOH + 4C = 5Na_2O + 3CO + CO_2 + 5H_2$ (absorbing 20 cals.).

In all 579 cals. are absorbed per 230 gm. of sodium or 112 gm. of fixed nitrogen, and thus the reaction theoretically absorbs 5,160 cals. (= 6 k.w.h.) or 1·52 kg. of coal per kilogram of fixed nitrogen. The flue gases contain 797 + 64 + 19 + 29 + 49 + 30 = 988 cals., or 8,820 cals. of calorific power per kilogram of fixed nitrogen. In addition, a further small amount of coal is used corresponding to the reduction of the ferrous oxide above mentioned.

The figures obtained above by calculation for the energy requirements cannot be attained in practice. They assume the use of chemically pure materials and do not allow for losses. Impurities, more particularly moisture, entail increased requirements of coal ; heat losses occur by radiation, conductivity and so forth, owing to the high temperature of the flue gases and of the cyanised product. The radiation losses in particular would be reduced to a minimum by working with the largest possible units. On the other hand, only small furnaces yield good results at the low working temperatures.

The heat carried away by the flue gases is small, as their

temperature is considerably below 100° C. Heat losses in the form of steam are also unimportant.

"We arrived at the conclusion that the energy requirements are 10 k.w.h. or less per kilogram of fixed nitrogen, apart from furnace losses. There should be no serious practical difficulty in constructing a furnace the radiation losses from which would amount to 25 to 50 per cent., in which case the consumption of energy would be 12 to 15 k.w.h. per kilogram of fixed nitrogen."

Barium oxide and soda are equally effective as bases. Barium oxide requires a cyanisation temperature which is about 100° higher, but is less sensitive to overheating, as the compound which is produced, $BaO.Ba(CN)_2$, is very stable. In consequence of the lesser alkalinity of barium compounds, less durable materials may be used for the furnace walls than in the case of soda. When using barium carbonate it is unnecessary to add iron, the addition of which may give rise to many difficulties. If the production of ammonia alone is required, the use of barium carbonate is always preferable. The use of soda, on the other hand, greatly increases the possibilities of disposing of the cyanised products, as it is easy in that case to obtain pure sodium cyanide, ferrocyanide, formate, oxalate, formic acid, oxalic acid, formalin, oxamide and so forth.

If the cyanisation process is considered as a method of fixing nitrogen and producing ammonia, it presents a closed cycle of operations in which ammonia, carbon monoxide and hydrogen are manufactured from nitrogen, coal and water. The carbon monoxide and hydrogen are burnt and utilised for heat production. In practice, therefore, the cycle amounts to a synthesis of ammonia from nitrogen and the hydrogen of water, which takes place according to the following equations, and may be compared with the water-gas process :—

$$\begin{array}{l} Na_2CO_3 + 4C + 2N = 2NaCN + 3CO, \\ 2NaCN + 4H_2O = Na2CO_3 + H_2 + CO + 2NH_3 \\ \hline 4C + 2N + 4H_2O = H_2 + 4CO + 2NH_3. \end{array}$$

According to Thorssell, the cyanide process is considerably cheaper and very much easier to carry out than the Haber-Bosch process. In comparison with those of other nitrogen fixation processes, the capital costs are especially low. Moreover, the process offers the valuable feature that by-products may be obtained in the form of valuable organic compounds, which are produced synthetically, as is the ammonia itself. The cyanisation process does not produce either nitrogen compounds only, or organic substances only, such as calcium cyanamide, but both nitrogen compounds and organic compounds simultaneously, and requires much less energy.

When producing nitrogen by passing air over a heated mixture of soda and spongy iron, Thorssell noticed that masses of carbon often separate during the reducing phase, according to the equation:

$$2CO = CO_2 + C.$$

Thorssell does not refer to Bucher's work on this particular matter. On opening the retort in these cases he always found a more or less strong smell of ammonia. This formation of ammonia is due to the fact that the mixture of soda and iron, coated with finely divided carbon, immediately reacts with nitrogen to form cyanide, which in turn reacts with the water vapour in the moist outer air, when the hot retort is emptied, with formation of ammonia. Thorssell uses this reaction to improve his original process, producing ammonia continuously from carbon monoxide and steam by passing these over a mixture of soda and catalytic iron. In working according to this process the conditions must be so arranged that the yield and the reaction velocities enable it to be carried out economically. Ammonia must be produced at a temperature below 600° C., as otherwise the ammonia which is formed would be decomposed to a considerable extent. On the other hand, the separation of carbon must also take place at the same low temperature. Thorssell has found that this separation is influenced as follows by high pressures:—

Pressure.	$t = 627°$. Per cent. of CO.	$t = 550°$. Per cent. of CO.
1 atm.	57	20
10 ,,	24	7
100 ,,	8	2

As cyanisation is promoted by increased pressure, which also reduces the decomposition of ammonia, it is better to carry out the whole process under pressure. The process takes place according to the following equations:—

(1) $Na_2CO_3 + 4C + 2N = 2NaCN + 3CO$ (iron contact).
(2) $2NaCN + 4H_2O = Na_2CO_3 + H_2 + CO + 2NH_3$,
(3) $4CO = 2CO_2 + 2C$

(4) $2C + 2N + 4H_2O = H_2 + 2CO_2 + 2NH_3$.

The problem had to be solved of carrying out reaction (1), which is favoured by a temperature of about 950° C., in such a manner that it occurs at 500° to 600° C. at as rapid a rate as the two other reactions, namely, the decomposition of carbon monoxide and liberation of ammonia.

H. Lundén studied the effects of various temperatures on cyanisation in the case of other alkalies and alkaline earths in the laboratories of the A.B. Kväfveindustri. He found that the necessary

temperatures are directly proportional to the boiling points of the corresponding metals and indirectly proportional to their atomic weights. He was unable to find any connection between the cyanisation temperatures and the melting-point of the salts which were used, as he had previously assumed. Thorssell communicates Lundén's results in the following table :—

	Li.	Na.	K	Rb	Cs.	Ca.	Sr.	Ba
Boiling point of the metal.	1,400° C.	880° C.	760° C.	696° C.	670° C.	--	—	1,000° C. (approx.)
Temperature of reaction.	1,100° C	930° C.	830° C	700° C. ?	600° C. ?	1,600° C.	1,400° C.	1,050° C.
Product	Cyanide.		Cyanide.		—	Cyanamide.	Cyanamide + cyanide.	
Energy requirements in kilowatt hours per kilogram of nitrogen.	—	10	10	9 ?	8 ?	16	15	13
Temperature of volatilisation of the cyanide.	900° C.	1,000° C.	1,000° C.	?	?	?	?	1,150° C.
Possibility of producing the metal by reduction with carbon.	Impossible.	Possible.	Possible.	Possible.	Possible.	Impossible.	Impossible.	Impossible.
Temperature of carbide formation.	700° C.	—	Not obtainable under these conditions.			1,800° C.	?	1,600° C.

This table leads to the conclusion that in the cases of rubidium and cæsium cyanisation occurs at low temperatures at such a rate that the plan above suggested could be carried out. The temperatures to which an interrogation mark is appended have not so far been experimentally confirmed. It is known that in his original experiments Bucher also worked with rubidium.

Thorssell also followed Bucher's example by studying the electrolytic decomposition of molten sodium cyanide. He reconverted metallic sodium into cyanide with the help of carbon and nitrogen and converted cyanogen gas into oxamide containing 30 per cent. of nitrogen. At the close of this publication he refers to the following fellow-workers: A. Kristenson, H. Lundén, G. Frisell, E. Ljunggren, Göransson, T. Holmgren, Chr. Beck-Friis, O. Troell E. Edlund and E. Karlsson.

There are numerous patents due to J. E. Bucher and the Nitrogen Products Company, of Providence, Rhode Island.[1] According to French Patent 455,799, pure nitrogen is obtained by blowing air over wood charcoal heated to 780° C. in a muffle furnace, and is then passed over a heated mixture of graphite, finely divided iron and

[1] *Chem. Zentralbl.*, 1919, ii., 740; iv., 360.

soda. French Patent 453,086 deals with the further reactions of cyanide so obtained. German Patent 286,086 of December 15th, 1912, describes the principle of the whole process.

According to U.S. Patent 1,116,559, cyanisation and distillation *in vacuo* of the finished cyanide from the reaction mass, may be carried out in the same plant. U.S. Patent 1,120,682 contains a description of the reaction furnace which we have already described in detail. According to U.S. Patent 1,138,190, the vapour of an alkali metal is passed over iron-carbon contacts in a current of nitrogen at a temperature above 500° C., and cyanide is so obtained. U.S. Patent 1,138,191 describes in detail the manufacture of ammonia by hydrolysis of cyanides, whilst U.S. Patents 1,241,919 and 1,241,920 describe the manufacture of urea from alkali cyanate, ammonia and carbon dioxide.[1] According to the U.S. statistics for 1919 [2] the following quantities of soda, cyanide and other products were manufactured :—

	Manufactures.				Exports in Short Tons.	
	1918.		1919.		1918.	1919.
	Short Tons.	Million Dollars.	Short Tons.	Million Dollars.		
Sodium carbonate, Na_2CO_3	1,390,628	35·635	981,354	29·824	119,217	50·481
$Na_2CO_3.H_2O$ and sesqu-carbonate . . .	22,678	0·483	30,796	0·711	—	—
Sodium carbonate containing $10H_2O$ . . .	82,465	2·020	74,200	22 082	6,358	5,563
Sodium cyanide and sodium peroxide . . .	9,077	5 361	9,196	4·558	—	—

In German Patent 321,662 the A.B. Kväfveindustri, Göteborg (Sweden), describes a process of removing the impurities which accumulate in the reaction mass on operating the cycle of processes, due to the ash of the coal. When this mass is decomposed and the ammonia driven off, the acid impurities, such as alumina, silica, and so forth, combine with the alkali or alkaline earth oxides. These compounds may be decomposed by a stronger acid, which must contain C, H, O and N only, or it may be causticised if alkalis have been used, by means of lime, by which means silica, alumina and so on are rendered insoluble and the soluble constituents are returned to the cycle. Carbon dioxide is the most suitable acid, or if alkaline earths

[1] *Metall. Chem. Eng.*, **17**, 661 (1917); also *Zeitsch. f. angew. Chem.*, **1918**, ii., 98.
[2] *Chem. Ztg.*, 1920, p. 812.

have been used, formic or acetic acid. According to German Patent 325,878, iron is added in the form of oxalate or hydroxide.

In a lecture to the Technical Association of Göteborg on April 20th, 1920,[1] Thorssell states that not more than 12 k.w.h. are required in the electric furnace for the fixation of 1 kg. of nitrogen. The A.B. Kväfveindustri started to operate on an industrial scale in 1920. In April, 1920, only a very small portion of the plant was working, and the output capacity was therefore so small that no definite figures could be given. At that time there was also a shortage of power. In the interval the product of the Göteborg plant had appeared on the market. The extent to which this fertiliser will compete with the product of the Norsk Hydro on the Swedish market will naturally depend on its price and value. According to German Patent 300,812, the reaction mass consists of 50 parts by weight of barium cyanide, 40 parts of barium oxide, and 12 parts of carbon. On treatment with water the excess of barium hydroxide first crystallises and the remaining solution of barium cyanide is decomposed in autoclaves at a high temperature.

The electric furnace was resorted to owing to the continued high price of fuel. As stated in a communication of the A.B. Kväfveindustri,[2] a report by foreign experts confirmed the view that the process could be operated satisfactorily with the furnaces which were adopted. In future the cyanide process will undoubtedly be able to compete successfully with other processes of nitrogen fixation. The company decided to amalgamate with the A.B. Trollhättan Cyanidverk,[3] founded with a capital of 500,000 kr. The latter company owned works at Trollhättan, which were suitable for the chemical treatment of cyanide products such as were obtained by the A.B. Kväfveindustri. They also disposed of 2,050 kw. of electric power. By the acquisition of these works it is hoped that the manufacture at Göteborg will be further simplified. Moreover, various patents of the Trollhättan Company, which deal with nitrogen fixation, are important and valuable for the A.B. Kväfveindustri. After the amalgamation these works utilised the Thorssell process, but the manufacture of ammonium sulphate, the purification of sodium cyanide and the manufacture of by-products is also contemplated. 6,500,000 kr. of new capital are required, of which 4,000,000 kr. are to be obtained by the issue of new shares. As it was found impossible to obtain this amount, only 700,200 kr. being subscribed, the A.B. Kväfveindustri ceased operations for the time being.[4]

[1] *Chem. Ztg.*, 1920, p. 815.
[2] *Zeitsch. f. angew. Chem.*, 1920, ii., 414.
[3] *Chem. Ztg.*, 1916, *Chem. Techn. Übers*, p. 825.
[4] *Metallbörse*, 1920, p. 2063; *Zeitsch. f. angew. Chem.*, 1920, ii., 460.

In the economic section of this work we referred to the erection of a Dutch plant to operate a cyanide process by the Stikstofbindings-Industrie "Nederland." It is clear from a report on the condition of the Dutch chemical industry in the second quarter of 1920 [1] that very favourable results were obtained with this plant, and that it was hoped that the difficulties would shortly be overcome. Attempts are now being made to utilise the oxygen, which is obtained as a by-product, on a large scale. The manufacturing difficulties have not yet been completely overcome.

The A.B. Cyanid [2] was formed in Stockholm with a capital of 300,000 kr. in order to operate a process by A. R. Lindblad, which was developed by the Sandsta Elektriska Smältverk for the manufacture of alkali cyanide, ammonia and other products. In German Patent 293,904 (Norwegian Patent 30,880), Lindblad describes an electric furnace for carrying out the synthesis of cyanide from potash, coal and nitrogen. The main feature of the furnace is the prevention of the molten alkali from dropping out of the charge. Fig. 27 shows a vertical section. The hearth, 1, is connected above with the shaft, 2. Current enters through the electrodes, 3, which are surrounded by water-cooled sleeves, where they penetrate the masonry; 5 and 6 are inlet pipes for the gas. The cyanide, which escapes in vapour form with the flue gases, is condensed in 7. The furnace is charged through 8, whilst 9 is an outlet for gases.

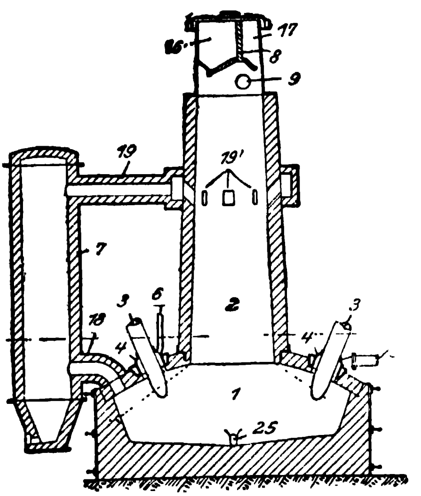

FIG. 27.

The manufacture of potassium cyanide is carried out, for example, as follows :—

The raw materials are K_2CO_3 or KOH and wood charcoal. Nitrogen is most simply obtained by fractionating liquid air. The wood charcoal is added through division 16 of the charging hopper and the potash through division 17. Nitrogen is introduced at the same side as the potash through tube 5, which enters through a pocket surrounding the electrode, where it serves the purpose of cooling the latter without any consequent heat loss. The electrode, 3, comes into

[1] *Metallbörse*, 1920, No. 45, p. 1759 ; *Zeitsch. f. angew. Chem.*, 1920, ii., 454.
[2] *Chem. Ztg.*, 1915, p. 600.

contact with the charge at a point where it is neither in contact with the inner walls nor the roof of the furnace. By this arrangement, any chance of the current passing through the masonry is avoided, although this latter becomes conductive at the cyanisation temperature. The mass is heated to such an extent that the cyanide formed according to the equation,

$$K_2CO_3 + 4C + 2N = 2KCN + 3CO,$$

is at once volatilised and carried off with the carbon monoxide. It passes through the main, 18, into the condenser, 7, where the KCN condenses and is collected. The accompanying gases are either withdrawn or passed back into the furnace through the flues and ports 19 and 19′. Wood-charcoal ash and slag are withdrawn through 25. The same furnace is used for the manufacture of NaCN, but other plant is better adapted for such high temperatures as are necessary for the manufacture of barium cyanide. According to German Patent 311,864, lime or basic compounds containing lime are added to the charge, and felspar and similar minerals are used as a source of alkali. In order to obtain alkali cyanide from felspar, this is crushed and mixed with coal and with sufficient lime to form a readily fusible slag. An electric furnace is then charged with the mixture. A portion of the potash is reduced according to the equation,

$$K_2O + C = 2K + CO.$$

The potassium which is liberated combines with carbon and nitrogen with production of potassium cyanide, which is carried off with the gases and recovered by condensation. The alumina and silica of the felspar form a slag with the lime which is tapped in the usual manner.

A. V. Lipinski, of Zürich,[1] has erected a small experimental works at Baden, Switzerland, for the manufacture of potassium cyanide by his electro-chemical process, but nothing further has so far been heard of the matter. In case favourable results were obtained, the manufacture was to have been started in 1917.

The experiments of A. Stähler [2] on the synthesis of cyanide in an electric high-pressure furnace are extremely interesting, and particularly important in view of Thorssell's results. The direct synthesis of cyanide from the alkali or alkaline earth oxides or carbonates, carbon and atmospheric nitrogen can be carried out particularly easily in an electric high-pressure furnace at a temperature of about 2,500° C. and a pressure of about 50 atm. Mixtures of alkali carbonate and carbon in rather more than the calculated proportion of the latter scarcely react at all to form cyanide when

[1] *Chem. Ztg.*, 1917, p. 166.
[2] *Ber.*, **49**, 2292 (1916).

heated at the ordinary pressure. On increasing the pressure, however, to 60 atm., 95 per cent. of the carbonate is converted into cyanide. Stähler also produced lithium cyanide with an 80 per cent. yield on the lithium compound employed.

According to German Patent 287,006 of A. Lang, briquettes are made from 87 parts of barium nitrate and 32 parts of coal, and are then fired. A reaction then occurs according to the following equation :—

$$8C + Ba(NO_3)_2 = 5CO + BaO + 3C + N_2.$$

When the upper part of the cartridge has burnt away, the mixture of nitrogen and carbon monoxide from the remainder passes over the red-hot residue of BaO and C. Cyanogen gas or cyanide is thus formed, the use of which for fumigating closed apartments and so forth is suggested.

In German Patent 318,286, Karl Prinz zu Löwenstein and F. Hauff propose to mix barium carbonate with carbon obtained, for example, by heating methane, to briquette the mixture and to treat these briquettes with nitrogen in rotary kilns at 1,200° to 1,400° C. The decomposition of the methane supplies not only carbon but also hydrogen, which is used for the production of nitrogen by burning in air.

The alkali amides (German Patent 316,137) have long been used for the manufacture of cyanide. O. Matter (German Patent 302,561) claims that a 90 per cent. yield of sodium azide can be obtained by treating sodium amide with nitrous oxide.

In German Patent 261,508 the Nitrogen Company, of Ossining, describe the manufacture of alkali cyanide from barium, carbon, nitrogen and alkali metal. According to U.S. Patent 1,052,815, Ch. J. Greenstreet obtains nitrogen compounds, such as cyanides, from red-hot hydrides of the alkaline earth metals, nitrogen, coal and sodium chloride or ferric chloride. O. Frank and O. Fincke pass nitrogen at 700° to 1,000° C. over an intimate mixture of iron and silicon or boron with lime, magnesia, or barium oxide (U.S. Patent 1,101,424). By working in the presence of several bases, they claim that melting of the reaction mass can be avoided, thus maintaining the activity of the surface layer. According to U.S. Patent 1,112,893, calcium cyanamide can be converted into a product suitable for the extraction of gold ores by melting with sodium sulphide, sodium chloride, and coal. 10 grams of $CaCN_2$, 5 gm. Na_2S, 5 gm. NaCl and 2 gm. of powdered coal, when heated to 800° to 1,000° C. in the absence of air, form a product containing 55 per cent. of cyanide according to the equation :—

$$2NaCl + Na_2S + 2CaCN_2 + 2C = CaCl_2, CaS + 4NaCN.$$

In U.S. Patent 1,143,952 H. Freeman proposes to purify crude cyanide by treatment with freshly precipitated ferrous hydroxide according to the equation,

$$6KCN + Fe(OH)_2 = K_4Fe(CN)_6 + 2KOH.$$

The ferrocyanide is purified by recrystallisation and then treated with alkali metal in a vessel filled with molten lead according to the equation,

$$Na_4Fe(CN)_6 + 2Na = 6NaCN + Fe.$$

B. Broch (Norwegian Patent 31,292) prepares alkali cyanide from alkali metal, nitrogen, and coal.

We have already referred to the attempts to synthesise pure hydrocyanic acid gas in the arc. E. Briner and A. Baerfuss have recently obtained good results with mixtures of nitrogen and methane.[1] The South Metropolitan Gas Company obtain ammonia by the hydrolysis of ammonium sulphocyanide (German Patent 321,661).

Cyanides and hydrocyanic acid play an important part in the destruction of animal and vegetable pests.[2]

In his reports of 1917, which are distinguished by the objective standpoint and wide knowledge which they display, Ch. L. Parsons expresses himself in favour of the cyanide process. His opinion [3] is that nitrogen can be more cheaply fixed in this form than by any other synthetic process, "and that this process will one day be of great importance in the world's nitrogen market, and will compete very seriously with other processes in consequence of the simplicity of method of operation and low constructional costs, but that the furnaces require great improvements." The Nitrogen Products Company is working on the development of the Bucher process under the supervision of Edward E. Arnold. In 1917 there were two small experimental plants, one at Saltville, Va., with a coal-fired furnace, and the other at Niagara Falls with an electric furnace. Both plants were inspected in April, 1917, by an American Government Commission.

In *Chem. Weekblad.*, **16**, 270 (1919),[4] M. J. F. Haarsma reports favourably on the cyanide processes, of which he states that the working costs are exceptionally low, and maintains that they are certainly capable of meeting competition.

[1] *Chem. Ztg.*, 1920, *Chem. Techn. Ubers*, p. 86.
[2] *Zeitsch. f. angew. Chem.*, 1919, i., 162 ; 1920, i., 85, 111, 117
[3] Hesse-Grossmann, "Englands Handelskrieg," vol. iii. (1919). pp. 85, 96.
[4] *Engineering*, January 30th, 1920, p. 157.

Supplement, 1921–24.

Judging by the results of the Thorssell plant at Gotenberg and the Bucher plant in the United States, which have so far been relatively unfavourable, it is probable that in the future cyanide processes will only be used for the production of ammonia in exceptional cases, but may become of importance for the manufacture of cyanide as such. The following patents by A.B. Kväfveindustri (Göteborg), Thorssell, Lundén and Lindblad describe developments in the production of cyanide: German Patents 321,662, 325,878, 331,230, 335,240; French Patents 523,139, 523,140, 531,688; British Patent 175,517/1921; Swiss Patent 95,037; and Norwegian Patents 31,662, 35,050, 30,880. There are detailed articles on the economics, etc., of the Bucher process by F. E. Bartell, M. de Kay Thompson, Ferguson and Manning in *Chem. Age*, **1922**, vi., 100; *Journ. Ind. Eng. Chem.*, **9**, 233; **11**, 946; **14**, 516, 699; *Chem. Met. Eng.*, **26**, 124, 1922. According to these, 1 lb. of cyanide in the form of briquettes costs 10 cents. German Patents 329,660, 332,580 and 334,145 of the Nitrogen Products Company, Providence, Rhode Island, dealt with further developments of the process. U.S. Patents 1,379,187, 1,388,586 and 1,422,878 of the Air Reduction Company, A. Kaufmann and J. T. Metzger describe a revolving furnace for the production of cyanide. The American Cyanamide Company, G. H. Buchanan and F. H. Washburn have worked on the manufacture of HCN from the melt obtained from calcium cyanamide and sodium chloride (U.S. Patents 1,355,384 and 1,398,453). The Norsk Hydro obtains ammonium formate from barium cyanamide according to British Patent 143,850/1921; Norwegian Patent 34,668; and German Patent 369,370. Other cyanamide processes are described in Norwegian Patents 34,430, 31,292; U.S. Patents 1,355,642, 1,397,613, 1,417,702, 1,386,941, 1,390,533; French Patent 538,512; British Patents 194,026/1921, 192,791/1921; and German Patents 348,068, 323,656.

Very important experimental work on the cyanisation of a highly compressed mixture of barium carbonate and wood charcoal at 1,300° to 1,400° C. in fifteen to thirty minutes (65 per cent. cyanide) has been carried out by Askenasy and Grude (*Zeitsch. f. Elektrochem.*, 130 (1922)).

On magnesium cyanide, see *Helv. Chim. Acta*, v., 396 (1922), and also German Patent 339,302 and *J. Am. Chem. Soc.*, **42**, 2663 (1920).

On the production of HCN in the electric arc from acetylene and nitrogen, see *Zeitsch. f. Elektrochem.*, 202 (1922); German Patent 348,208; and French Patent 504,853. The following publications

on hydrocyanic acid and its use for the destruction of pests are of interest: German Patents 332,297, 341,672, 358,124, 327,289; U.S. Patents 1,444,300, 1,408,757; British Patent 174,364/1922.

Interesting studies have been carried out by Bertelsmann on the scrubbing of HCN from the gases produced by dry distillation (*Journ. f. Gasbeleuchtung*, **62**, 205; see also German Patents 328,829, 321,661; U.S. Patents 1,413,762 and 1,413,763).

CHAPTER XXII

The Production of Nitrogen and Hydrogen

A DESCRIPTION of the processes of the nitrogen industry would be incomplete did it not describe the methods of preparation of the gases used as raw materials.

The cyanamide, nitride and Haber-Bosch processes require pure nitrogen, whereas the synthetic production of cyanides may sometimes use producer gas and similar gases. In processes which depend on the decomposition of primary products—more particularly calcium cyanamide, aluminium nitride and cyanides—by water, the hydrogen of the latter forms a constituent of the resultant ammonia. On the other hand, the Haber-Bosch synthesis requires free hydrogen to be combined with the nitrogen to form ammonia. It is therefore important for the nitrogen industry to manufacture pure nitrogen and pure hydrogen by the most economical methods possible. The synthetic processes to be described later, namely the manufacture of nitric acid by the electric arc, by the explosion of combustible gases and by the oxidation of ammonia in the presence of catalysts, utilise either air or ammonia as raw materials, so that no prior manufacture is necessary.

In the sections dealing with the cyanamide industry and with the cyanide processes, we already discussed various methods of manufacturing nitrogen, by passing air over briquettes containing iron and alkali, or by burning hydrogen in air. The most modern method of producing nitrogen, and the cheapest if large quantities are required, is by the rectification of liquid air. It is, of course, impossible for us to go into details here, and we must content ourselves with a short summary and by mentioning the newest patents and researches. Muhlert,[1] v. Unruh,[2] and Auerbach [3] have written on this subject both in the form of summaries and of periodical reports.[4] On December 24th, 1877,[5] Cailletet [6] reported to the Paris Academy that he had obtained a misty precipitate of oxygen by expanding that gas adiabatically in a glass tube, after first bringing it to a high

[1] "Die Industrie der Ammoniak und Cyanverbindungen" (Leipzig, 1915), pp. 46–54.
[2] Ullmann's "Encyclopædia," vol. vii. (1919), pp. 637–667.
[3] *Ibid.*, vol. v. (1917), pp. 679–702.
[4] *E.g.*, *Chem. Ztg.*, 1913, No. 110 *et seq.*; 1914, p. 494; 1915, No. 118 *et seq.*; 1919, No. 131 *et seq.*; 1920, No. 102 *et seq.*; pp. 847 *et seq.*
[5] According to C. Linde.
[6] *Compt. rend.*, **85**, 1216.

pressure and cooling it to $-29°$ C. by means of liquid sulphurous acid. Simultaneously a telegraphic report was handed in from Pictet according to which he had succeeded in obtaining a stream of liquid oxygen from his receiver. He had cooled oxygen to a low temperature in two stages, with liquid SO_2 and liquid CO_2, at 200 atm. pressure, and then allowed it to escape. These first experiments had proved the possibility of liquefying oxygen, but no one had then succeeded in producing large quantities, maintaining it in a liquid condition and studying its properties. At a later date Cailletet pre-cooled the gas by evaporating liquid ethylene at $-105°$ C., but made no essential progress. In 1883, v. Wroblewski and Olszewski [1] described and employed apparatus in which the gas was pre-cooled by evaporation of ethylene at 2·5 cm. pressure and $-139°$ C. In the same year Cailletet [2] demonstrated his apparatus for continuous working. All these processes depended entirely on cooling, produced step by step by the evaporation of volatile materials, namely liquid carbon dioxide and liquid ethylene and oxygen, and so rendered it possible to carry out the numerous investigations on the physical behaviour of liquid gases which we owe more particularly to Olszewski and later to Dewar, who succeeded the preceding experimentalists in 1884, and who brought the same principle of the evaporation of liquefied gases to a high degree of perfection.

C. Linde has described Dewar's experiments [3] of 1884 in detail in a small published summary on "Maschinen zur Erzielung niedrigster Temperaturen, zur Gasverflüssigung und zur mechanischen Trennung von Gasgemischen" (Machines for the Attainment of the Lowest Temperatures, for the Liquefaction of Gases and the Mechanical Separation of Gaseous Mixtures). In 1895 [4] Olszewski determined the critical constants of hydrogen. Dewar obtained liquid hydrogen in quantity in 1899.[5] Attention has recently been drawn in the *Chemikerzeitung* of 1920 to work of Perkins, previous to 1823, on the liquefaction of gases.

The forms of laboratory apparatus used by Cailletet, Pictet, Olszewski and Dewar were entirely unsuitable for working on a large scale, the possibility of which was considered at an early date. The solution of the problems in question was attained by distinguished technologists. In 1885 E. Solvay obtained a patent for "an apparatus for obtaining extreme temperatures," in which he proposed to produce and liquefy gas in the cold. His principle of working is identical

[1] *Compt. rend.*, **97**, 1115.
[2] *Ibid.*, **96**, 1140; *Wiedem. Ann.*, **20**, 243.
[3] *Phil. Mag.*, **18**, p. 212.
[4] *Wiedem. Ann.*, 1895.
[5] *Chem. News*, 18 (1899), p. 132.

with that for which W. Siemens had already applied for a provisional patent specification in 1857. This depended on a combination of a cold-air machine of the usual type with a heat exchanger, in which the temperature drop obtained in the working cylinder, due to adiabatic expansion, was transferred to the compressed air destined to undergo subsequent expansion. This principle was retained or rediscovered, not only by Solvay, but also by various other patentees. The train of thought is quite correct theoretically, but in practice it would always be found that, as Cailletet stated before the Paris Academy on behalf of Solvay in December, 1895, "the lowest temperature which I was able to attain was - 95° C., as beyond that point the losses of cold predominated over its production."

At the end of May, 1895, C. Linde demonstrated and explained a working machine to a circle of physicists, chemists and technologists in Munich, which consisted of an air compressor and two heat exchangers only, and which was able to produce several litres of liquid air hourly. This new Linde apparatus depended on the principle of removing heat from the gas to be liquefied by the production of internal work, until the temperature dropped below the critical temperature and condensation was effected. The principle of the Linde process is described in German Patent 88,824 of June 5th, 1895, and the other foreign patents: British Patent 12,528/1895, U.S. Patents 727,650, 728,173, and Swiss Patent 10,704, and was thus established independently of the preceding patents already referred to, of Siemens (British Patent 2,064/1857) and Solvay (German Patent 39,280/1883). The invention is described as "a process and a machine for the liquefaction of air, essentially for the purpose of carrying out the separation of gaseous mixtures such as air." This aim was first expressed by Linde. We will further describe the Linde process later.

Simultaneously and independently of Linde, Hampson [1] utilised the Joule-Thomson effect and the counter-current principle as the bases of his technical process which is described in British Patent 10,165/1895 and U.S. Patent 620,312. The Hampson apparatus is of no more industrial significance than the very convenient demonstration apparatus of Heylandt (see below), which is described in German Patent 236,454/1909.

In contrast with the apparatus and processes above described for the liquefaction of air by the production of internal work there are others which effect the liquefaction with production of external work. According to this system the gases are only allowed to expand by driving the piston of an expansion engine or rotating a turbine. The

[1] M. v. Unruh, *loc. cit.*, pp. 652 *et seq.*

necessary power for this work is withdrawn from the expanding gas in the form of its heat equivalent, so that the gas is necessarily cooled. The mechanical work which is produced supplies a portion of that which is necessary for compression, and can be utilised as recovered power for raising the efficiency of the plant as a whole.

After many unsuccessful attempts [1] G. Claude was the first to succeed in constructing a machine on this principle which worked successfully at − 140° to − 150° C., and was lubricated with petroleum spirit. The maximum pressure used is 45 atm., and it is not necessary to cool the air much below its critical temperature of − 141° C. The main features of the process are described in French Patent 296,211, Patent of addition 2,885, British Patent 12,905/1900 and Austrian Patent 8,305. This process has not been used to any extent in Germany, but "L'air liquide, Sociétè Anonyme pour l'Etude et l'Exploitation des Procédés Georges Claude," of Paris, has introduced the process very successfully in France, Italy, America and other countries for the manufacture of liquid air, oxygen, nitrogen, argon, and other products. The Linde Company has acquired the sole constructional rights for Claude plants in Germany. A licence has also been granted to the Chem. Fabrik Griesheim-Elektron.

The process of Mewes relies on similar main principles and is protected by several patents, the first being German Patent 119,943/1901 in the name of Metz. An experimental installation [2] produced 14 to 15 litres of liquid air per hour in 1913 after 2 to 2½ hours from starting and with an expenditure of 87 h.p., of which 10 to 12 h.p. were recovered from the expansion engine.

Pictet's system for liquefying and rectifying air, described in German Patents 162,702/1901, 165,268/1901 and 169,564/1901, has not proved successful in practice. Several Pictet plants have been built and started in Germany and abroad by the Sauerstoff-Industriegas A.G. of Berlin, for instance at Borsigwalde, Hanover and other places. After the company had gone into liquidation, the plants were rebuilt according to the Linde system. Whereas Linde and Hampson use throttle valves only, and Claude, Pictet and Mewes only use expansion engines, Heylandt combines both systems in an extremely effective process, using both internal and external work.[3] The construction of the expansion engine in a manner which had hitherto been considered quite impracticable is characteristic of this

[1] See more particularly Kausch, "Herstellung, Verwendung und Aufbewahrung flussiger Luft," 5th edition (Weimar, 1919).

[2] *Zeitsch. f. Sauerstoff und Stickstoff*, 1914, pp. 23. 47.

[3] This statement must be accepted with reservation, as Claude, for example, utilises both the internal and external work of expansion.—TRANSLATOR.

process, which is described in German Patents 191,659/1906, 270,383/1908, and others. This plant is supplied by the Gesellschaft für Apparatebau P. Heylandt m.b.H., of Berlin-Mariendorf. The liquid air which is produced contains 80 to 85 per cent. of oxygen. Bernstein [1] gives the following figures relating to experimental runs of twenty-four hours :—

	Production.	Energy Required per Litre.
Heylandt plant .	25 litres of liquid air per hour containing 85 per cent. oxygen.	1·4 to 1·5 k.w.h.
Linde plant .	,, ,, ,, ,, ,,	2·6 to 2 8 k.w.h.

The superiority of the Heylandt system is somewhat less in plants for the production of oxygen or nitrogen, in which the power requirements are only 20 to 25 per cent. lower than those of Linde plants of the same output.

The following figures by M. v. Unruh [2] show the industrial distribution of plants of these various systems in 1919 :—

Oxygen Production in cu. m. in Germany.

In 1900	about	30,000
,, 1909	,,	2,000,000
,, 1913	,,	13 000,000
,, 1919	,,	65,000,000

	Cu. m. of Oxygen.
Annual production of Linde plants .	45 to 50 million.
Annual production of Heylandt plants	14 ,, 15 ,,
Annual production of Claude plants	4 ,, 5 ,,

The Gesellschaft für Lindes Eismaschinen A.G., at Höllriegelskreuth, near Munich, gives the following figures for total plant delivered or under construction up to October, 1918 : 209 oxygen plants with an annual output capacity of 72·5 million cu. m. ; 55 nitrogen plants of an annual output capacity of 310,000,000 cu. m. ; 18 hydrogen plants on the Linde-Frank-Caro system of an output capacity of 29,000,000 cu. m. ; and 120 liquid air plants.

We will now give a short and comprehensive description of the Linde plants for the liquefaction and rectification of air.

The raw material is atmospheric air, as free as possible from dust,

[1] *Glückauf*, 1915, No. 51.
[2] *Loc. cit.*, p. 637.

which contains on the average about 21 per cent. of oxygen and 79 per cent. of nitrogen. The critical temperature of air is — 141° C. The boiling points of liquid oxygen, at — 183° C., and of liquid nitrogen, at — 195·8° C., are sufficiently far apart to enable liquid air to be separated into these constituents in a rectifying column. The products of this rectification are evaporated and heated to the ordinary temperature with partial recovery of the cooling effect used for their liquefaction.

The air is first brought to the necessary high pressure which is initially 120 to 200 atm., but which can be reduced when the apparatus is working continuously to 40 to 80 atm., at which pressure the radiation losses are just neutralised. After removing the heat of compression by cooling water, the compressed air is allowed to expand to atmospheric pressure through a throttle valve. In consequence of the deviation of the properties of compressed air from those of an ideal gas, compressed air has a lower heat capacity than uncompressed air at the same temperature, and consequently, if the release of pressure takes place by means of a throttle valve in such a manner that heat cannot be absorbed from the surroundings, a cooling effect is produced, known as the Joule-Thomson effect; this cooling effect amounts to about 40° to 50° when starting at an initial pressure of 200 atm. at room temperature, that is about 0·25° C. per atmosphere of pressure difference.

If the released cold air is carried in counter-current to the entering compressed air in a heat exchanger, the temperature of the air supplied to the throttle valve is continuously reduced. The air at the outlet of the throttle valve attains a correspondingly lower temperature until finally the temperature of liquefaction is reached. The heat abstraction produced by the release through the valve now liquefies a portion of the air.

As already mentioned, the separation depends on the difference of the boiling points of oxygen and nitrogen. If liquid air is gradually evaporated, the vapours which are first formed contain more nitrogen than the liquid which is being evaporated, the oxygen contents of which consequently increase. It is, however, impossible either to obtain pure nitrogen free from oxygen in this matter or to obtain practically pure oxygen in such a yield as would render the process practical.

In order to obtain oxygen of the necessary purity the evaporation would have to be carried so far that only a small fraction of the oxygen originally present would remain in the pure state.

A practically complete separation is only achieved with the help of the Linde rectification process described in German Patent

173,620. According to this process the vapours escaping from the evaporating liquid air are washed with liquid air in a column. In this way, on the one hand, the escaping vapours are washed until they contain as much oxygen as suffices to restore equilibrium with the liquid which enters, namely, 7 per cent., if this latter is liquid air; on the other hand, the descending liquid becomes steadily richer in oxygen on passing down the column until finally the necessary purity is attained.

In order to remove the remaining 7 per cent. of oxygen in the escaping gases, the liquid air is replaced, according to German Patents 180,014 and 203,814, by pure liquid nitrogen, which is obtained by a previous rectification at higher pressure; this is used as the washing liquid in an upper rectification column. By this arrangement it is possible to obtain nitrogen of 99·9 per cent. purity; if, on the other hand, the rectification is intended primarily for the production of oxygen, a by-product can be obtained in this way consisting of nitrogen of more than 97 per cent. purity, and thus an extremely favourable yield of oxygen may be obtained. Oxygen is usually manufactured of a strength of 98 per cent., but its purity can be raised to 99·8 per cent.

The exchange of heat between the air which enters and the oxygen and nitrogen leaving the apparatus is practically complete, so that the separated gases leave the apparatus at almost the same temperature as that at which the compressed air enters. During continuous working, that is when the apparatus has once been filled with liquid, it is therefore only necessary to produce a sufficient cooling effect to cover the inevitable losses due to heat absorption from the warmer neighbourhood by means of radiation and conduction. This smaller cooling effect requires a lower degree of compression than is initially necessary, and in the case of larger plants during steady working the pressure can be reduced to 30 atm. Instead of compressing the whole quantity of air to this pressure a specially favourable utilisation of energy is achieved by compressing a portion only to a higher pressure of 100 to 200 atm., whilst the larger portion enters the apparatus at 5 atm. pressure only. Such plants are described as systems with separate high and low pressure air supply.

Before entering the liquefaction column the air must be freed from carbon dioxide and water vapour, as these impurities separate as solids at low temperatures and would, if not removed, lead to blockage of the tubes. Carbon dioxide is removed by washing with caustic soda solution, and water vapour by absorption by calcium chloride or by pre-cooling. Apart from the drying effect on the air, such pre-cooling serves a further purpose, namely a shortening of

the cooling period in the separating column and an increase in the cooling effect, that is a decrease in the power requirements for a given output of the plant, in consequence of an increase in the cooling effect at the throttle as the temperature of entry is lowered.

A Linde plant for the manufacture of nitrogen and oxygen therefore consists essentially of the following parts :—

(1) The liquefaction and rectification column ;
(2) The compression plant ;
(3) Plant for drying and purifying the air ; and
(4) Usually a pre-cooling plant.

The liquefaction and separating column contains the counter-current column and the rectification column. Both are mainly constructed of copper and bronze, which are the only materials suitable at such low temperatures. They are covered with a thick layer of heat-insulating material, such as silk, and contained in a stout wooden casing.

The air is compressed by multi-stage compressors of two to five stages, according to the final pressure to be attained ; at each stage the air is cooled with water in order to remove the heat of compression. The absorption of carbon dioxide is effected either by interposing a scrubbing tower in the air inlet main, which is fed with caustic soda solution by a centrifugal pump, or the air may be passed at high pressure through a high-pressure iron container filled with caustic soda solution, in which suitable baffles effect intimate contact between the air and the liquid.

The pre-cooling of the air is effected by a liquid ammonia refrigerating plant which cools the air in a counter-current heat exchanger to about -30° C. by the evaporation of liquid ammonia. The evaporated ammonia is compressed and reliquefied by cooling with water. When the air is cooled the water-vapour which it contains separates as ice, which adheres to the walls of the apparatus. After a certain period the tubes of the pre-cooler become blocked with ice, and it must then be withdrawn from the circuit and warmed. For continuous working two pre-coolers are therefore necessary, which are used alternately.

The installations are intended for continuous working. Apart from occasional longer stoppages for overhauling of the machinery, it is necessary to stop the plant at regular intervals of one or more weeks, according to its size and the efficiency of the purifying arrangements. At these intervals the ice and the solid carbon dioxide, which gradually collect in the separating column, have to be removed by warming, a procedure which requires about twenty-

four hours. The purifying system never works quantitatively, and therefore considerable quantities of ice and carbon dioxide accumulate during the working period. In order to shorten the periods of inactivity it is therefore desirable to maintain two plants which work alternately. When absolutely continuous manufacture is required, reserve machinery must also be erected. The Linde nitrogen plants of large modern works maintain at least one complete installation in reserve.

The following table gives the most usual sizes of nitrogen plants, together with their requirements for power and cooling water, and the approximate weight of the whole installation including one complete assemblage of units without reserve pre-coolers and other plant :—

Catalogue designation of plant	D3	H6	H8	H10	H12	H14	N12	N14	N20
Output in cu. m. of N per hour	40	120	200	400	800	1,600	800	1,600	4,000
Total power requirements in B.H.P.	36	60	85	160	305	580	210	400	950
Power requirements in B.H.P. per cu. m. Nitrogen	0·9	0·5	0·43	0·40	0·38	0·36	0·26	0·25	0·24
Consumption of cooling water in cu. m. per hour	1	3	4	7	13	25	12	24	55
Approximate weight in tons	11	16	24	37	68	100	64	105	180
System	A. High-pressure air only.					B. High-pressure and low-pressure air.			

On account of the somewhat complicated arrangements of the installations with both high- and low-pressure air the advantages afforded by them in reducing the power requirements only become apparent for large installations. The power requirements given in the table represent power applied at the shaft of the engine ; the cooling water is supposed to enter the plant at a temperature of 15° C.

The output mentioned in the second line of the table is the quantity of gas in cu. m. at the ordinary temperature (17° C.) and at the same pressure at which it reaches the compressors, that is at the prevailing atmospheric pressure. The weights of oxygen and nitrogen consequently alter according to the temperature and pressure of the air at the intake, so that when the temperature is very high or the barometer low, the output becomes correspondingly smaller. If, in such cases, it is necessary to maintain a standard weight of output of oxygen or nitrogen, the pressure at the intake must be raised to 1 atm. by the use of a fan or the intake air must be cooled to the required temperature.

The average purity of the nitrogen is 99·5 per cent. It is possible with a Linde plant to adjust the purity of the products within a fairly wide range. A corresponding alteration in the output is thus achieved; for example, instead of 100 cu. m. of oxygen of 98 per cent., one may obtain 110 cu. m. of 95 per cent. or about 95 cu. m. of 99 per cent. purity. Impurities in the gases consist essentially of oxygen, nitrogen and argon. The nature of the process excludes the possibility of other impurities; it is desirable that the gases should be absolutely dry.

The nitrogen obtained as a by-product in the manufacture of oxygen has usually a purity of 94 to 98 per cent., or of 92 to 93 per cent. in the case of plants up to, but excluding, size 4; the oxygen obtained as a by-product in the manufacture of nitrogen contains 60 to 80 per cent. of oxygen. It is, however, possible, with installations involving a comparatively small extra outlay, to produce pure nitrogen and pure oxygen simultaneously. In the case of nitrogen plants, pure oxygen can be obtained as a by-product to the extent of 20 per cent. of the nitrogen output. As the working costs are not appreciably increased by the simultaneous manufacture of both components, the by-products are obtained almost free of cost. If desired, limited quantities of liquid oxygen and liquid nitrogen can be obtained in addition to the normal manufacture.

We will now give a small table on the working costs of a Linde nitrogen installation assuming average prices of the year 1915:—

Output in cu. m. per hour . .		40	400	4000
Cost of power:—				
1 h.p. hour = 10 pfg. .	Mark	3·60		
1 h.p. hour = 6 ,, .	,,		9·60	—
1 h.p. hour = 1 ,, . .	,,		—	9·50
Wages per hour:—				
1 mechanic and 1 assistant	,,			
1 mechanic and 3 assistants	,,			3·80
Materials:—				
Lubricating oil . . .	,,	0·30	0·50	1·80
Caustic soda . . .	,,	0·10	0·30	2·50
Calcium chloride, water, cleaning materials, etc. . .	,,	0·10	0·40	1·50
Working costs per hour . .	,,	6·10	12·80	19·10
Working costs per cu. m. N .	Pfg.	15·2	3·2	0·48

It is naturally only possible to estimate the working costs accurately when the exact conditions are known. The above figures include neither amortisation nor interest on the plant, nor the cost

of any compression of the manufactured gases. The figures given for the 4,000 cu. m. plant are those with which the large nitrogen works in Central Germany have to deal. To-day these figures must be multiplied by at least 25 to 30. In 1917–18 one could still reckon on a production cost of 1·5 to 2 pfg. per cu. m. of nitrogen at the locality of manufacture.

The accompanying sectional diagrams indicate the principle of the liquefaction and rectification of air by Linde's process. The compressor (Fig. 28) causes air to enter at 200 atm. pressure at the upper end of the counter-current column. It traverses the innermost tube from top to bottom, where its pressure is reduced to 20 to 50 atm. by a reduction valve *a*. It then returns along the intermediate space between the internal and external tubing back to the top of

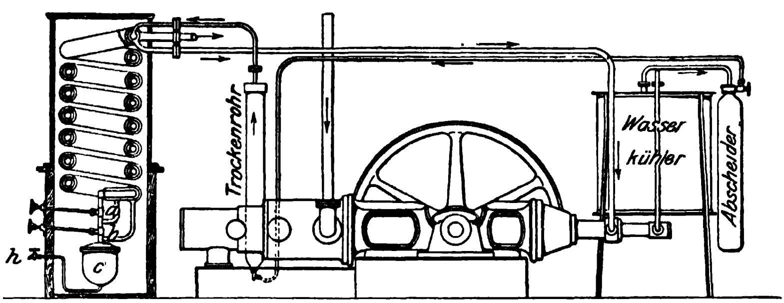

FIG. 28. Air liquefaction plant.

Trockenrohr = Drying tube. Abscheider = Water separator.
Wasserkuhler = Water cooler.

the system, where it is once more compressed and recirculates through the system. When continuous working has been established, the air which is utilised is replaced in equal measure from the outer atmosphere by entering through the valve *b*. Liquefied air assembles in *c*, from which it may be withdrawn through *h*.

The next figure (Fig. 29) shows a Linde rectifying column for the manufacture of oxygen or nitrogen. The compressed air, which has been reduced to approximately its temperature of condensation in the counter-current spiral, *A*, enters the heating coil, *D*, which is immersed in a bath filled with enriched liquid air, and is here liquefied. The surrounding liquid is partially evaporated by this process. The vapours rise in the column *B*. The pressure of the liquid air is reduced to the pressure in the column, which is 3 to 5 atm., by the reduction valve, *H*, and falls through the ascending vapours. The oxygen content of these is thus reduced to 10 per cent. They ascend further up the column and condense in *F*, which is

immersed in the evaporating vessel, *E*, of the second column, which contains liquid oxygen boiling under atmospheric pressure. The condensed liquid now flows partially back through the first column and removes oxygen from the vapours ascending the same until these contain about 4 per cent. only of that gas. The descending liquid is thus enriched until it contains about 50 per cent. of oxygen, and flows into *C*. Its pressure is then reduced to atmospheric pressure by the reduction valve, *O*, and it enters the second column, *G*, about half-way up. The rest of the condensed gas, containing 4 per cent. of oxygen only, is reduced to atmospheric pressure by the valve, *N*, and carried to the top of the second column. The oxygen is evaporated from *E* through the condensation of the vapours enriched with nitrogen from the first column, and rises in *G*. The oxygen which is produced leaves the column *E* below and traverses the counter-current apparatus, whilst the nitrogen leaves the column *G* at *e*, also passing through the counter-current heat exchanger.

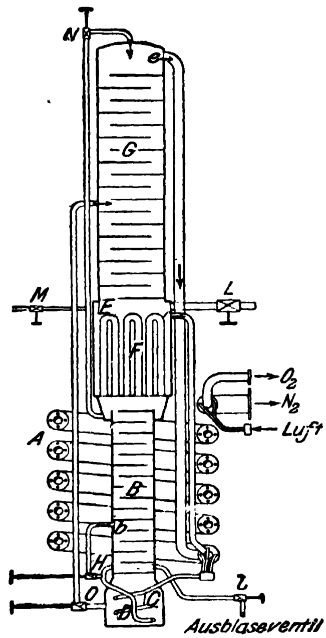

FIG. 29.
Ausblaseventil = Blow-off valve.
Luft = Air.

The form of apparatus just described serves for the manufacture of oxygen. If it is to be used for producing nitrogen, the proportion of vapour to quantity of liquid is reduced in both columns and the oxygen is thus more completely removed. In the lower column, which is maintained at a higher pressure, this is achieved by increasing the quantity of liquid which is returned to the column; in the upper column the same purity is achieved by passing a larger proportion of the vapours through the oxygen tube below the column. The by-product has in this case a strength of 60 to 80 per cent. The columns are constructed entirely of copper and bronze with the help of solder as these metals only are sufficiently tough at the temperature of working. Slag wool and silk waste are used as insulating materials.

Numerous pamphlets are issued by the Gas Liquefaction Department of the Gesellschaft für Lindes Eismaschinen A.G., Höllriegelskreuth, near Munich, and others have been published by the inventor, C. v. Linde. The most important and modern of these are a pamphlet

containing a description of such installations and working instructions for same, printed as a pamphlet in Munich in 1918; a small pamphlet, entitled "Lowest Temperatures in Industry"; a volume by C. v. Linde, "Technik der tiefen Temperaturen" (Munich, 1913); an article in the *Zeitsch. d. Ver. Deutsch. Ing.*, 1900, p. 69; and lectures by the inventor at the Forty-third Annual Meeting of that Association at Düsseldorf in 1902 and at the Fourth Annual Meeting of the "Deutsches Museum, Munich," at Berlin in 1907.

The small volume, "Lowest Temperatures in Industry," was presented to the participants of the Third International Refrigeration Congress at Chicago, 1913, by the Linde Company. It is of especial interest here, as it gives good illustrations of the nitrogen plants at Trostberg and Odda, and also an excellent general view of the last-named works.

In his paper on the Utilisation of Liquid Air in Industry, which Linde read to the *Zeitsch. d. Ver. Deutsch. Ing.* in 1900,[1] he already referred to the utilisation of oxygen-enriched air in gas producers and so forth. If oxygen could be obtained sufficiently cheaply, he states that such uses would constitute the most valuable of all applications of the liquefaction of air. He refers to the proposals in this direction which were made by Hempel,[2] and also to the prize which was offered by the Verein zur Förderung des Gewerbefleisses [3] arising out of these proposals. These suggestions are based on the assumption that 1 cu. m. of 50 per cent. oxygen can be manufactured at 1·2 pfg. at the pre-war rate of exchange; the production cost of pure oxygen in plants of an output of 1,000 cu. m. per hour in 1915 was 1·91 pfg. The publication of Linde, above referred to, contains a drawing of a gas producer for the gasification of low-grade fuel with the help of enriched air. These processes are of far greater interest to-day, as the nitrogen industry now produces oxygen as a by-product for which a use is sought.[4]

Large modern nitrogen fixation works often utilise more than 200,000 cu. m. of air per twenty-four hours, from which they obtain about 150,000 cu. m. of pure nitrogen and 60,000 cu. m. of 60 to 70 per cent. oxygen. This latter escapes, in many cases, entirely or partially into the air without further utilisation. Considerable quantities of oxygen are utilised for the autogenous welding of metals, for oxygen rescue apparatus, and in other branches of industry.

[1] *Loc. cit.*, p. 69.
[2] *Chem. Ind.*, 1899, No. 1.
[3] *Sitz Ber.*, 1899, p. 92, "Untersuchung der mit konzentriertem Sauerstoffe—(Linde—Luft)—gewonnenen Generatorgase."
[4] *Sudd. Ind. Blatt*, 1919, p. 2805; *Chem. Ztg.*, 1919, p. 859; 1920, p. 39; 1921, No. 9 *et seq.*

It has also uses in other industries,[1] a number of promising suggestions having been made in connection with more intensive illumination,[2] and also in metallurgy [3] and for the production of aluminium, calcium carbide,[4] and other products, quite apart from the use of enriched air in the gasification of low-grade fuels, which has already been referred to.

The German cyanamide works manufacture the nitrogen which they require almost exclusively by Linde's process, whilst the works at Oppau and Leuna obtain a part of their requirements by other methods which will be discussed later under the heading of hydrogen manufacture.

It is impossible to consider the refrigerating industry and further details of the patent literature of refrigerating machines and so forth in this book. We must content ourselves with a few considerations on the Linde process of liquefaction [5] and the newest patents of the Linde Company, which are concerned with the production and rectification of liquid air, namely, German Patents 281,761, 289,106, 295,654, 301,940, 301,941, 302,674, 319,344, 319,992 and 321,241.

A description of a Heylandt installation with section and elevation was published by Albrecht in the *Technische Rundschau*,[6] a supplement to the *Berliner Tageblatt*. Numerous other recent patents have been granted to R. Mewes, H. Runge, H. Barschall, Sprengluft G.m.b.H., of Charlottenburg, Industriegas G.m.b.H., in Berlin, and others (see German Patents 282,665, 286,764, 290,809, 294,485, 312,286, 312,639, 313,800, 317,889, 321,819, 322,138, 324,661, etc.). For the production of nitrogen on a very small scale, Siemens and Halske A.G. propose, in German Patent 286,514, the use of a nitrogen alkali compound such as potassium nitride mixed with tantalum powder, which is strongly heated. In German Patent 314,171, Siemens-Schuckert-Werke G.m.b.H. propose the use of high-tension electric currents for the purification and separation of gases. E. Herman (German Patent 303,881) burns methane with air in such quantity that carbon dioxide, nitrogen and hydrogen are produced, the latter arising from the pyrogenic decomposition of methane.

Among the various attempts which have been made to utilise the nitrogen of flue gases those of Frank and Caro deserve special attention, as they have led to an interesting manufacturing process.

[1] *Chem. Ztg.*, 1920, p. 848.
[2] *Ibid.*, 1915, "Repertorium," p. 297.
[3] W. Mathesius, "Die physikalischen und chemischen Grundlagen des Eisenhuttenwesens" (Leipzig, 1916), pp. 277–278; see also *Chem. Zentralbl.*, 1920, iv., 604.
[4] *Zeitsch. f. Elektrochem.*, 1902, p. 349.
[5] *Journ. Franklin. Inst.*, 177 (1914), 305; *Chem. Ztg.*, 1915, p. 299.
[6] September 29th, 1920, No. 21.

N. Caro[1] describes this process, which is claimed in German Patents 183,702 and 204,882, as follows: "Flue gases obtained by the combustion of coke or coal under boilers and consisting of a mixture of nitrogen, CO_2, CO, oxygen and hydrocarbons, are completely converted into a mixture of carbon dioxide and nitrogen only, by passing over a mixture of copper and copper oxide in a special manner. This gas is washed with water under pressure, which removes the carbon dioxide, leaving pure nitrogen undissolved." In German Patent 311,438 J. Muchka proposes to manufacture a mixture of nitrogen and carbon dioxide, containing but little oxygen, from the gases of a combustion motor. According to British Patent 20,667/1913, L. P. Basset separates sulphur dioxide and carbon dioxide from flue gases with the aid of sodium sulphite, sodium carbonate and other compounds.

We have already referred to the attempts of the Lonza A.G. to utilise the ease with which ammonium sulphite is oxidised for the manufacture of atmospheric nitrogen. It is said that this process is to be used on a manufacturing scale. It is described in German Patents 302,671 and 316,502. Cyanamide ammonia is caused to react with pyrites burner gases to form ammonium sulphite, a solution of which can be smoothly oxidised at 70° to 75° C. by passing an air current through it. For example, 48 kg. of the sulphite were converted into sulphate in six hours with the production of 22·4 kg. of nitrogen containing 0·1 to 0·2 per cent. of oxygen only. The B.A.S.F. has claimed a similar process in German Patents 273,315 and 276,490 and British Patent 12,845/1912. For example, they treat concentrated, slightly ammoniacal ammonium sulphite solution with air at 20 atm. pressure at 80° C. in presence of porous tiles coated with manganese hydroxide. A. Stutzer (German Patent 255,439) claims the oxidation with pure oxygen at 100° C., but as undiluted oxygen is used the process is of no interest to us here. The principle embodied in the Lonza patent is also to be found in E. Collett's German Patent 283,161 and in German Patent 283,618 of the Höchster Farbwerke in a somewhat modified form. H. Hultman's Norwegian Patent 30,822 claims a somewhat similar process.

German Patent 321,241, French Patent 471,162 and British Patent 15,053/1914 are due to l'Air Liquide, of Paris.[2] This company, which operates the Claude processes, has for some time possessed works at Paris, Le Havre, Nantes, Pont Ste. Maxence, Audincourt, Lyons, St. Chamond and Marseilles, and has erected new oxygen works at Rouen, St. Nazaire, Bordeaux, Nancy and Hénin-Liétard.

[1] "Aus Luft durch Kohle zum Luftstickstoffdünger usw.," 1920, p. 17.

[2] See L. Kolbe, "Flüssige Luft, Sauerstoff, Stickstoff, Wasserstoff" (Leipzig, 1920). (An extended translation of G. Claude's book.)

It is strongly represented outside France. In America it is closely connected with the Air Reduction Company, which has combined with the National Carbon Company and the Union Carbide Company, with a total capital of $200,000,000, in order to carry out the production of liquid gases and other processes.

The works at Muscle Shoals include a Claude plant. This is housed [1] in a building 30·5 × 175 m. in dimensions, which lies 400 m. east of the cyanamide works, in order to ensure pure air at the intake. This is aspirated by centrifugal blowers through two mains 914 mm. in diameter, which end in two openings north and south of the east side of the building and 490 m. distant. The aspirated air is passed through 8 units, each containing two scrubbing towers, 9·15 m. high and 2·44 m. in diameter, which are fitted with spiral contact rings 152 mm. in diameter, down which caustic soda solution of 17° Bé. trickles. The caustic soda effluents are regenerated in the ammonia works. The actual liquefaction plant comprises 15 duplex three-stage compressors, which pass the air into 30 nitrogen columns at 25 atm. pressure. The three stages of compression are 2·5, 10, and 15 atm. Twenty-four columns work simultaneously, whilst six remain in reserve. They contain a series of horizontal pans, 38 mm. deep, filled with liquid air, through which the expanding gases are caused to bubble. The compressed air is released to a pressure of about 6 atm., and performs work during expansion by driving a small motor of 4 to 5 h.p. Ninety per cent. of the air passes into the rectifying column at − 140° C., whilst 10 per cent. passes directly into the column at 25 atm. and liquefies the pre-cooled remainder, which collects at the base of the column. The gas which is thus enriched with nitrogen meets a stream of liquid nitrogen which enters at the top of the column, so that the gas leaves the column containing 99·9 per cent. of nitrogen and at a pressure of 254 mm. of water. The oxygen passes through a heat exchanger and is then rejected.

A high-pressure main with 5 two-stage Sullivan compound air pumps is connected directly to the liquefaction plant ; this aspirates the air through a 760 mm. conduit and distributes it throughout the works at 8 atm. pressure. In this way 930 cu. m. of air are compressed per minute.

The Swiss works manufacturing liquid air in Lucerne, Berne, Turgi, Lenzburg, Rumlang, Schaffhausen and other places had a pre-war output of 400,000 to 500,000 cu. m. of oxygen which has had to be doubled in consequence of the large demand. New oxygen works have been erected at Basle, Vevey, and other places.

[1] *Chem. Met. Eng.*, **8**, 1920, (1919).

In England the first plant for the production of liquid air was erected in 1907. At the commencement of 1918 there were only 8 such plants and 2 further plants which manufactured oxygen by means of barium peroxide. In 1919, 118 tons of liquid air were being produced daily, 85 per cent. of the oxygen from which was used for welding and 15 per cent. for medical purposes; there are individual installations in Germany which liquefy about 260 tons of air daily. In Hungary, Denmark, Sweden, Norway, Holland, Russia, Australia, Japan and other countries the liquid gas industry has become firmly established.

The Société Générale des Nitrures has a Claude plant producing 300 cu. m. of nitrogen per hour at St. Jean de Maurienne, and 16 other installations each producing 400 cu. m. of nitrogen per hour are said to be in use in the production of cyanamide. The first Linde installation at Odda produced 375 cu. m. per hour, and that at Trostberg 700 cu. m. per hour. Before the war six further installations were used for cyanamide manufacture, each with an output capacity of 125 cu. m. per hour.

Among the many industrial applications of liquid air and its products,[1] we may refer more particularly to liquid air explosives,[2] which have been the incentive to great improvements in methods of storage and transport of liquid air and liquid oxygen.

According to H. Erdmann,[3] 1 cu. m. of dry atmospheric air contains :—

				Gr.
9·41	litres of	argon .	. weighing	16·76
0·012	,,	neon .	. ,,	0·011
0·004	,,	helium .	. ,,	0·0007
0·000,05	,,	krypton	. ,,	0·000,19
0·000,006	,,	xenon .	. ,,	0·000,035

The development of gas-filled electric incandescent lamps containing the rare gases [4] has caused the production of these gases as by-products of the liquefaction of air to be profitable. Thus the American Cyanamide Company produce argon as a by-product of their nitrogen plant [5] and have marketed it since December, 1914.

The Chem. Fabrik Griesheim-Elektron [6] passes commercial oxygen mixed, for example, with hydrogen over a catalyst consisting of copper, platinum or palladium, according to German

[1] *Chem. Ztg.*, 1918, p. 483.
[2] *E.g.*, *Chem. Ztg.*, 1920, p. 743, *Chem. Techn. Übers*, p. 219; *Chem. Zentralbl.*, 1919, iv., 696.
[3] "Lehrbuch der anorganischen Chemie," 5th edition, 1910, p. 234.
[4] *Chem. Zentralbl.*, 1918, ii., 90; 1919, iv., 139; *Elektrotechn. Zeitsch.*, 1919, p. 149.
[5] *Chem. Ztg.*, 1915, pp. 113, 220.
[6] *Umschau*, 1920, p. 739; *Chem. Ztg.*, 1918, 429.

Patent 295,572. The residual argon is freed from nitrogen by absorption with magnesium or by fractional rectification. The Linde Company describe a process for the manufacture of argon in German Patents 301,940 and 311,958. In an ordinary liquid air rectifying column a portion of the rare gases contained in the air collects at the upper part of the condenser (*F* in Fig. 29, p. 535) and causes an increase in the pressure of the column. It thus becomes necessary to open a cock commonly known as the " Helium " cock in order to allow these gases to escape and normal pressure to be restored. R. Brandt treats this gaseous residue with calcium in order to purify the rare gases (German Patent 314,907). G. Claude [1] obtains a mixture of oxygen and nitrogen with a relatively large proportion of argon as a middle fraction in the rectification of liquid air. This mixture is liquefied at a suitable pressure by a bath of liquid oxygen with return flow of the condensed liquid. During this process the nitrogen, being the most volatile constituent, escapes. Argon is removed by fractionation from the mixed liquid so obtained at a concentration of 75 to 80 per cent., the rest consisting of oxygen and 1 to 2 per cent. of nitrogen. The oxygen is easily removed by chemical means. M. Bodenstein and L. Wachenheim [2] have developed an interesting laboratory method on the basis of this process, which is described in German Patent 295,572. The Hydroxygen A.G., of Budapest, commenced to manufacture argon in 1916, and the Bureau of Yards and Docks, Navy Department, Washington, was erecting a similar plant in 1919 at a cost of $430,000.

P. Siedler describes the manufacture of neon, which is used for filling the so-called glow lamps,[3] in the *Umschau*.[4]

It has already been mentioned, in describing the nitrogen industry in the United States, that the isolation of helium from gas wells and other sources is largely dependent on low temperature technology ; the first attempts to carry out this process industrially were made in that country.[5]

L. Bock describes an apparatus for liquefying ammonia in German Patent 305,916. W. Greaves contributes a comprehensive summary on the manufacture of liquid ammonia.[6]

The first Linde liquefaction plants were shown at the Exhibitions in Nürnberg, 1896, Munich, 1898, and Paris, 1900. In 1901 a larger

[1] *Umschau*, 1920, p. 739 ; *Chem. Ztg.*, 1918, 429.
[2] *Ber.*, 51 (1918), 265.
[3] *Zeitsch. f. angew. Chem.*, 1918, iii., 245 ; *Chem. Ztg.*, 1918, p. 187 ; *Elektrotechn. Zeitsch.*, 1919, p. 186 ; *Umschau*, 1919, p. 152 ; *Chem. Zentralbl.*, 1920, iv., 673.
[4] *Umschau*, 1920, p. 466.
[5] *Chem. Ztg.*, 1919, pp. 271, 527, 604, 767, 799, 867, 887 ; *Chem. Zentralbl.*, 1920, iv. 431 ; *Umschau*, 1920, p. 141 ; *Chem. Zentralbl.*, 1920, iv., 603, 673.
[6] *Chem. Zentralbl.*, 1919, iv., 177.

experimental plant using 150 h.p. was erected at Höllriegelskreuth to enable the rectification of liquid air to be studied in greater detail, and in 1903 the first industrial oxygen plant was erected there with an output capacity of 10 cu. m. per hour. The total hourly output capacity of all the German installations was 20 cu. m. in 1903 and 835 cu. m. at the end of 1913. In 1913 the joint output of all Linde plants in the world was 15,104,000 cu. m. of oxygen. The process of the Linde Company for manufacturing hydrogen was developed at a later date than those for manufacturing oxygen and nitrogen.

In German Patent 174,324 A. Frank, N. Caro and A. R. Frank describe a process of obtaining pure hydrogen from dry water gas, which latter they pass over calcium carbide at a high temperature.

From gas of the composition—

50	per cent.	H_2
40	,,	CO
5	,,	CO_2
4·5	,,	N
0·5	,,	O

they obtain in one stage a gas containing 99 to 99·6 per cent. of hydrogen; the nitrogen is fixed as cyanamide and the CO, CO_2 and oxygen are also fixed with formation of calcium oxide, calcium carbonate and graphite. Although this method attained no practical importance, the suggestion passed on by A. Frank to the Linde Company in 1909, that they should endeavour to apply low temperature methods to the preparation of hydrogen from water gas, fell on very fruitful soil. With the co-operation and subsequent support of the Berlin Anhaltischen Maschinenbau A.G., of Berlin, the Linde-Frank-Caro process was evolved and was protected by German Patents 254,043 and 261,735 and by Swiss Patent 56,594; the process was first described by the Linde Company, F. Pollitzer [1] and F. Linde.[2] Up to October, 1918, 18 hydrogen plants had been erected on this system with a total output capacity of 29,000,000 cu. m. of hydrogen. Further details on the development of the process will be given later.

The average composition of water gas is:—

48 to 52	per cent.	H_2
42 ,, 44	,,	CO
5	,,	CO_2, and
5 ,, 3	,,	N_2.

It also contains varying amounts of oxygen, methane and

[1] *Zeitsch. d. Ver. Deutsch. Ing.*, 1912, pp. 1540 *et seq.*
[2] *Zeitsch. f. angew. Chem.*, 1913, iii., 814.

sulphur and phosphorus compounds. The boiling point of hydrogen which is 20·4 degrees absolute, and of carbon monoxide, which is 82 degrees absolute, are sufficiently far apart to render a separation of the two gases by fractional condensation conceivable unless the mutual solubility relations should prove to be unfavourable. If a mixture of equal volumes of hydrogen and carbon monoxide at atmospheric pressure is cooled to the boiling point of liquid air, no separation occurs. The partial pressure of liquid carbon monoxide is 0·5 atm. at − 197° C., and a lower temperature than this has to be attained before a portion of the carbon monoxide separates in liquid form. At − 205° C. the vapour pressure of liquid carbon monoxide is still $\frac{1}{7}$ atm., and at this temperature the escaping gas would still contain 14 per cent. of carbon monoxide. In order to obtain a more complete separation, either the temperature must be reduced still further or the gaseous mixture must be brought to a higher pressure. If, for example, the water gas is compressed to 50 atm., the partial pressure of the carbon monoxide at − 197° C. will be 0·5 atm. only, and the partial pressure of the hydrogen will be 49·5 atm.; thus the carbon monoxide contents in the remaining gas will be $\frac{0{\cdot}5}{50} = 1$ per cent. The proportion of carbon monoxide in the hydrogen would only be reduced to 0·3 per cent. at − 205° C. and 50 atm. pressure.

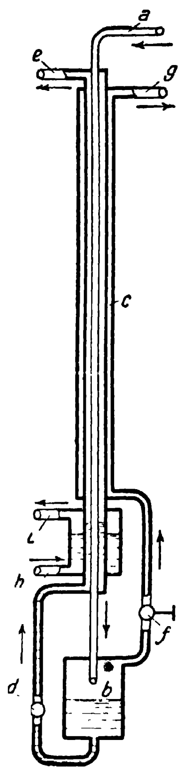

FIG. 30. — Diagrammatic representation of the separation of carbon monoxide and hydrogen.

It is not possible to cool water gas by simple expansion by the Linde process in the same manner as air. In consequence of the high percentage of hydrogen, the Joule-Thomson effect with this gas is very small—that is, it is only cooled to a very slight extent when the pressure is reduced. Liquid air must therefore be used as a cooling agent as in the condensation of hydrogen.

Fig. 30 shows the apparatus used for liquefaction in diagrammatic form. Compressed water gas enters the apparatus at *a*, and is cooled in countercurrent to the necessary low temperature by the escaping cold gases. Carbon monoxide is thus separated as a liquid and collects in vessel *b*. Its pressure is then reduced through the valve *d*, and it leaves the apparatus at *e* at the atmospheric temperature. The pressure of the hydrogen is reduced and it passes out

through *c* and *g*. The liquid air which is used for cooling to the low temperature required and also for compensating for radiation losses, is diagrammatically indicated at *hi*. Temperatures below that of boiling liquid air are obtained by expanding the compressed gases or by cooling with air boiling at a very low pressure. In the large-scale apparatus the heat-exchanging coils and the condensers for the liquefied gases are well insulated by wool or silk enclosed in a wooden casing.

The other impurities, such as nitrogen, which boils at – 196° C., are condensed with the carbon monoxide, which boils at – 192° C., and the gas which remains unliquefied is essentially hydrogen, which boils at – 253° C. As obtained it has the following composition:—

	Per cent.
CO_2, O_2, CH_4, and heavy hydrocarbons .	0·0
CO	2·0 to 1·7
N_2	1·0 „ 0·8
H_2	97·0 „ 97·5

The carbon monoxide fraction contains 80 to 85 per cent. of that gas. It is utilised in a gas engine and supplies the whole of the energy required by the plant. Instead of attaining the necessary very low temperature by using liquid air as such, it is still more economical to utilise liquid nitrogen boiling *in vacuo*. It is absolutely necessary previously to purify the water gas, and so remove the carbon dioxide. In order to save sodium hydroxide the greater portion of the carbon dioxide is now removed by water under pressure as suggested by Bedford. The gas so obtained contains 0·3 to 0·5 per cent. of carbon dioxide only, and is then treated as usual with sodium hydroxide solution, lime, etc.

In the case of installations producing 100 cu. m. of hydrogen per hour, the carbon monoxide fraction is sufficient to supply the whole of the power requirements. In larger plants an excess of power is available which may be utilised for separating the liquid air required for the process into pure oxygen or nitrogen in the same apparatus. This combination is particularly valuable for the purpose of the synthesis of ammonia or the welding of metals.

The hydrogen which is obtained has a specific gravity of 0·094 and is pure enough for most purposes connected with metal working, metallurgy or aeronautics. By passing it over soda-lime under pressure the remaining carbon monoxide can be quantitatively removed and the gas then contains 99·2 to 99·4 per cent. of hydrogen by volume and 0·6 to 0·8 per cent. of nitrogen. Its specific gravity is then 0·077 to 0·079, that of the chemically pure gas being 0·070 (air = 1).

The cost of hydrogen obtained by the Linde-Frank-Caro process naturally depends on the cost of raw materials, power, and so forth, and also on the size of the installation. Under normal pre-war conditions in a plant of average size 1 cu. m. of relatively impure hydrogen of 0·094 specific gravity cost 12 pfg. and 1 cu. m. of the purified gas of 0·077 specific gravity about 15 pfg. The complete removal of catalytic poisons is very important for purposes of fat hardening or for the synthesis of ammonia.

The following table gives a few data on the requirements of power and raw materials :—

Size of plant	I.	II.	III.	IV.	V.
A. For Hydrogen Manufacture Only.					
Hourly output in cubic metres of hydrogen . .	25	50	100	200	500
Hourly requirements in cubic metres of water gas .	70	125	250	500	1,250
Coke required in kilograms per hour . . .	50	80	160	320	780
Cooling water required in cubic metres per hour .	2 25	3·80	7·60	13·50	32·50
B. For the Production of Hydrogen together with Oxygen or Nitrogen.					
Production in cubic metres of hydrogen per hour .	10	20	40	100	—
Production in cubic metres of oxygen per hour .	3		10	25	—
Requirements of water gas in cubic metres per hour	50	80	150	300	—
Requirements of coke in kg. per hour . . .	40		95	190	—
Requirements of cooling water in cubic metres per hour	1·30	2 10	3·30	6 50	—

Fig. 31 represents a complete Linde-Frank-Caro plant diagrammatically.[1] Gas from the producer, *A*, is washed in scrubbers, *B*, and in the dryer, *C*, and collected in the gas-holder, *D*, which feeds the compressors, *E*. The gas, which still contains about 3 per cent. of carbon dioxide, is passed through towers, *F*, in which it is scrubbed with water after the first or second stage of compression. The remaining carbon dioxide is absorbed by caustic soda solution in the purifiers, *G*, after the final stage of compression. The water gas is then separated into its constituents in the two liquefiers, H_1, and H_2, each of which is used continuously in turn for one week. The hydrogen leaves these liquefiers at about 50 atm. pressure, thus saving a large part of the work which would otherwise fall to the compressor, *J*, which compresses the gas into the steel bottles, *K*. The five-stage compressor, *L*, with pre-cooler, *M*, serves for the liquefaction of air. The air is cooled with liquid ammonia produced by the ammonia compressor, *N*, and the condenser, *O*.

The carbon monoxide which is obtained as a by-product may be converted into sodium formate by combination with caustic soda or may simply be burnt. Plant for the hourly production of 200 cu. m. of hydrogen from water gas which is compressed to 60 atm.

[1] F. Pollitzer, *loc. cit.*

requires 260 h.p., including energy losses, whilst the carbon monoxide obtained as a by-product is capable of supplying 280 h.p., so that

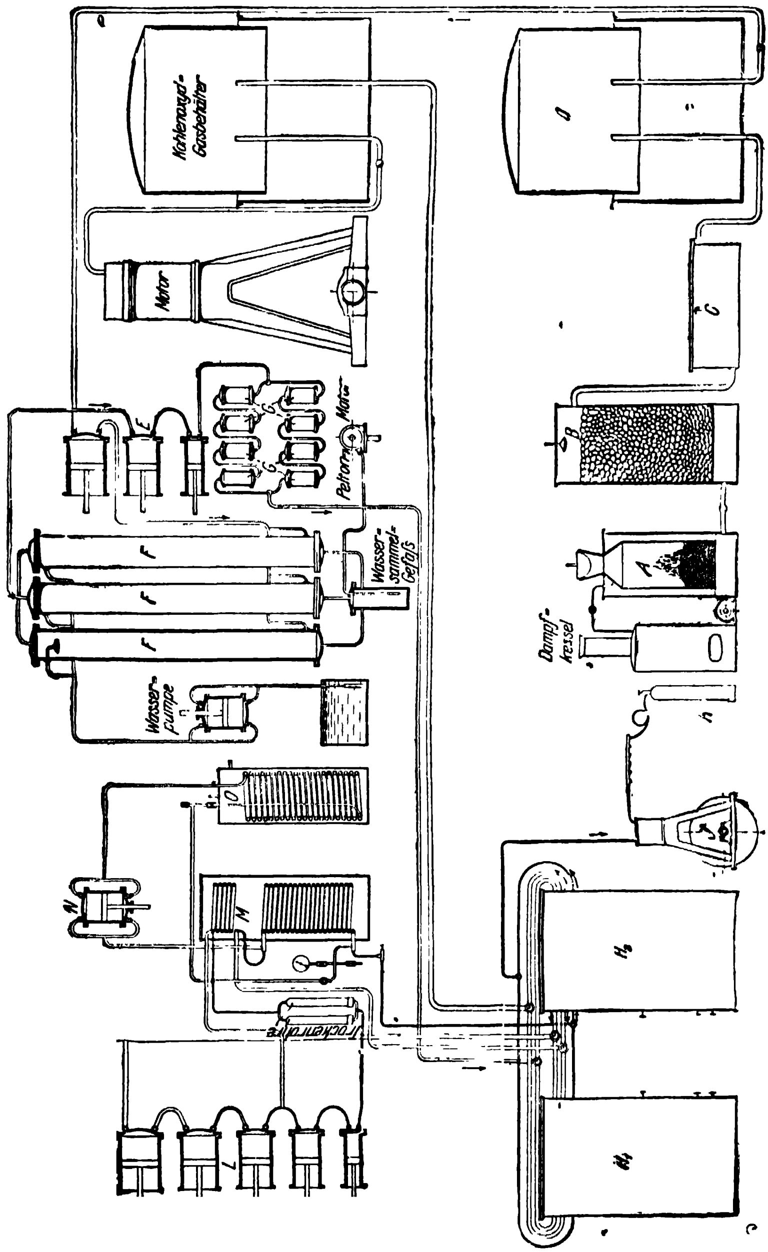

FIG. 31.

Trockenröhre = Drying tubes. Wasser-pumpe = Water pump. Wasser-sammel-Gefäss = Catch-pot.
Kohlenoxyd-Gasbehalter = Carbon monoxide gas-holder. Dampf-kessel = Steam boiler.

there is an excess of 20 h.p. The working of these hydrogen plants is very simple and almost automatic, so that installations of average

size require two to three workpeople only. According to Pollitzer the production cost per cubic metre of hydrogen in an installation producing 200 cu. m. per hour and under the price conditions of 1912 was 8 to 9 pfg. by the Linde-Frank-Caro process and 10 to 13 pfg. by the steam-iron process. The Linde-Frank-Caro process requires 1·8 kg. of coal and coke per cubic metre of hydrogen, whilst the steam iron process of the Internale Wasserstoff A.G. requires about 2·5 kg. for equal purity of hydrogen.

The first plant working on this new system was built by the dockyard of Blohm & Voss at Hamburg. The two following plants were erected for the Linde Companies at Vienna and Tegel. The next installations were for the provision of hydrogen for fat hardening: Wolgasche A.G. "Salolin," of St. Petersburg, 100 cu. m. per hour; Nijni Novgorod, 30 cu. m. per hour; Bremen Besigheimer Olfabriken, Bremen, 200 cu. m. per hour; Ver. Seifenabriken, Rotterdam, 200 cu. m. per hour; Ardol Co., Ltd., Leeds, 500 cu. m. per hour. The B.A.S.F. first built two small experimental installations for supplying the high pressure ammonia bombs, and after these had proved satisfactory a large installation was built for Oppau,[1] which started operation in the summer of 1913. In 1912 7 Linde-Frank-Caro installations were at work, with an annual output capacity of 2,000,000 cu. m. of hydrogen, 5 further installations were under construction, with an output capacity of 5·5 million cu. m., and one further installation had been ordered. German Patent 272,086 and French Patents 453,187, 475,297 and 475,346 of L'Air Liquide should also be referred to.

In the *Chemikerzeitung* of 1919, p. 745, the following summary is given of other processes of manufacturing hydrogen :—

Elektrizitäts A.G. vorm. Schuckert & Co., of Nürnberg: Capacity of plants erected, 18,000,000 cu. m. of hydrogen per annum.

Carl Francke, of Bremen (Messerschmitt process): Capacity of plants built since 1914, 68,000,000 cu. m. of hydrogen per annum.

Berlin Anhaltische Maschinenbau. A.G. (Bamag-Schacht process): Capacity of plants constructed up to the commencement of 1917, 110,000,000 cub. m. of hydrogen per annum.

Improvements in hydrogen manufacture have been summarised in numerous reports to which we may here refer.[2] Hydrogen can be produced on a large scale from iron and sulphuric acid, zinc and slaked lime, silicon and caustic soda solution, aluminium and caustic soda solution, ferro-silicon and caustic soda solution or soda lime,

[1] According to Claude, *Mém. Soc. Ing. Civ.*, 1913, p. 65, this had an output capacity of 2,000 cu. m. hydrogen per hour.
[2] *Chem. Ztg.*, 1913, No. 110 *et seq.*; 1915, No. 118 *et seq.*; 1919, pp. 745 *et seq.*; 1915, p. 144; *Chem. Zentralbl.*, 1920, iv., 385–386.

calcium hydride, by the electrolysis of water, from acetylene, by the decomposition of steam with iron and by other methods.

For the production of hydrogen for the synthesis of ammonia the Linde-Frank-Caro system and the steam-iron system are alone of importance. The Messerschmitt process, which is protected by German Patents 258,053, 263,390, 263,391, 266,863, 267,594, 268,062, 268,339, 274,870, 276,132, 276,719, 277,500, 284,532, 290,869, 291,603, 291,902, 297,900 and 306,314; French Patent 444,105, 444,106, 461,480; and British Patent 18,028/1913, depends on the alternate oxidation of metallic iron by steam and reduction of the oxide which is formed. This method has been exhaustively discussed by F. Müller.[1] The best results are obtained with bog iron ore from Siegerland. Roasted spathic iron ore, burnt pyrites or mixtures of these two are less satisfactory. A producer of 250 cm. external diameter holds 3,000 to 3,500 kg. of iron ore. This is reduced by water gas from a Dellwik-Fleischer plant. The producer is heated to 700° to 900° C. by water gas; this requires 7 to 8 hours in the first instance, but only 17 to 19 minutes during continuous working. When the whole charge is completely reduced it is scavenged with superheated steam for 5 to 10 seconds, in order to remove the last traces of water-gas and air, and the valves are then changed over. The steam which now enters passes over the red hot charge of reduced iron in the reverse direction, causing the following change to take place:—

$$Fe + H_2O = FeO + H_2.$$

The "make" period lasts for 8 minutes. As soon as this is over air is introduced for 3 to 5 minutes in order to oxidise all the carbon and any sulphur which may have been deposited, a process accompanied by considerable evolution of heat. The charge is now once more reduced by water gas. During the first days of working the charge of 3 to 3·5 tons produces 70 to 75 cu. m. of hydrogen at each "make" equal to 3,400 cu. m. of hydrogen in twenty-four hours, during which there are forty-seven "make" periods; the yield gradually decreases to 30 to 40 cu. m. of hydrogen per "make," or 1,650 cu. m. per twenty-four hours, owing to shrinkage of the reaction surface in consequence of sintering of the ore. With a charge of 3 to 3·5 tons of ore of good quality, a total of 60,000 to 100,000 cu. m. of hydrogen of an average quality of 98·9 per cent. can be obtained. The crude gas is cooled to 80° C. in a washing tower in which it is partially freed from CO_2 and H_2S; it

[1] *Zeitsch. kompr. flüss. Gase*, **20**, 4 (1919-20); *Chem. Ztg.*, 1920, *Chem. Techn. Übers*, p. 258.

then passes through a pressure equalising gas holder of 200 cu. m. capacity and then through several dry purifiers which are filled partly with iron oxide and partly with slaked lime. The hydrogen, when so purified, only contains small traces of CO, CH_4 and N.

The Bamag-Schacht process of the Berlin-Anhaltische Maschinenbau A.G. resembles the Messerschmitt process ; it partially depends on patents of the B.A.S.F. and is only used for large installations which produce more than 1,000 cu. m. per hour continuously ; up to July, 1918, the Bamag had supplied 75 hydrogen installations for an approximate output of 125,000,000 cu. m. per annum in execution of 47 orders and frequent repeat orders and 250 water-gas installations with a daily output of 2,500,000 cu. m. in execution of 160 orders and repeat orders. The installations supplied to the B.A.S.F. until the commencement of 1917 had an annual output capacity of 19·5 million cu. m. of hydrogen.

The hydrogen which is obtained can be purified up to 99·6 per cent. quality. It is free from detectable quantities of sulphur, arsenic and phosphorus compounds. The Bamag-Schacht process, which is described in German Patents 267,944 and 300,711, and in French Patent 465,474, differs from the Messerschmitt process in so far as any kind of iron ore can be used, for example, burnt pyrites. The average period of " make " is six minutes. The change over from the reduction to the oxidation stage takes place automatically by means of a regulated valve movement. Hydrogen of 90 per cent. purity is readily attained in such installations, but the difficulties of manufacture increase with the purity. It is, however, possible to obtain gas of 98·5 per cent. continuously from these very reliable Bamag plants, and its purity can, if necessary, be further increased. During the War the two firms mainly interested in hydrogen manufacture, namely, C. Francke, of Bremen, and the Berlin-Anhaltische Maschinenbau A.G., of Berlin, concluded certain agreements in order to avoid a collision of their interests.

These methods of manufacture have thus re-utilised the old reaction of Lavoisier, discovered by him in 1783. We can only mention here numerous patents referring to these processes, for example, those of S. Elworthy and H. Williamson, German Patent 164,721 ; Dellwik-Fleischer-Wassergas-Ges., German Patent 229,406 ; O. Dieffenbach and W. Moldenhauer, German Patent 232,347 ; Internationale Wasserstoff A.G., German Patent 244,732 , N. Caro, German Patent 249,269, and others.[1]

[1] See also O. Kausch, *Chem. Apparatur*, 1915, ii., 125 ; British Patent 147,235/1918, etc.

In German Patent 284,816 the Chem. Fabrik Griesheim-Elektron claims the action of steam at 10 atm. pressure at 600° to 800° C. on a mixture of lime and coal :—

$$C + 2H_2O = CO_2 + 2H_2.$$
$$CO_2 + CaO = CaCO_3,$$
$$CO + H_2O = CO_2 + H_2.$$

In German Patent 298,911 the Harburger Chemische Werke Schön & Co. and W. Daitz propose to utilise the carbon monoxide obtained by liquefaction from water gas, by burning it with air in such quantity that pure nitrogen remains, serving as a source of this gas. According to German Patent 303,931 S. Fränkel removes carbon monoxide from gaseous mixtures by washing them with a mixture of sulphuric and chromic acids activated with mercury or silver oxide or similar substances. J. Weise and F. Riecke propose to treat caustic soda with producer gas free from carbon dioxide, thus producing sodium formate and pure nitrogen. If the formate is heated it is converted into oxalate with liberation of hydrogen, which latter may be utilised for the synthesis of ammonia together with the nitrogen (U.S. Patent 1,098,139). According to U.S. Patent 1,123,394 mixtures of nitrogen and hydrogen of definite composition may be obtained by passing ammonia and air over copper turnings at 720° C.; H_2O, N_2 and H_2 are formed with decomposition of ammonia. In German Patent 319,763 G. de Grahl claims a process for the development of power by combustion of hydrogen.

For the production of nitrogen and hydrogen the B.A.S.F. uses the Linde process, the Frank-Caro-Linde process and the Bamag process ; it has also developed its own combined processes which are the subject of numerous patents.

According to British Patents 26,770/1913 and 27,117/1913 hydrogen is obtained from carbon monoxide and steam in presence of a catalyst at high temperature and pressure. In order to purify the hydrogen from injurious sulphur compounds and carbon monoxide before it enters the contact chambers, it is washed with 10 to 15 per cent. caustic soda solution at 150° to 225° C. and 50 atm. pressure (German Patents 254,344, 279,954 ; British Patent 14,509/1913 ; French Patent 439,262 and patent of addition 18,699).

Various further details of the catalytic process according to the reaction,

$$CO + H_2O = CO_2 + H_2,$$

are given in German Patents 279,582, 268,929 and 271,516. For example, a mixture of equal parts of ferric and chromium nitrates

are precipitated with ammonia, and the precipitated mixture of hydroxides is dried and moulded. It is then filled into the contact chambers, where the reaction between steam and carbon monoxide commences at 400° to 450° C. Carbon dioxide is readily removed by absorption. Another contact material contains oxides of iron, ammonium chromate and thorium nitrate. According to French Patent 463,114 pure hydrogen is obtained from methane and similar hydrocarbons by the action of a nickel catalyst at 700° C.

The contact process of the B.A.S.F. works smoothly and yields hydrogen of over 98 per cent. purity.[1] By starting with suitably adjusted mixtures of producer gas, water gas and steam this process may be used for the direct production of mixtures of nitrogen and hydrogen in suitable proportions for the synthesis of ammonia (German Patent 292,615). It is, however, important that the catalysts should be free from chlorine and sulphur compounds. Traces of these poisons may be absorbed by the addition of alkali to the contact carrier (German Patents 302,555 and 303,292).

The removal of the last traces of carbon monoxide is frequently impossible either by the contact method or by the Frank-Caro-Linde process. The B.A.S.F. therefore evolved a process of washing the hydrogen with solutions of cuprous oxide (*vide infra*).

According to German Patent 282,849 mixtures of iron, nickel and chromium oxides at 400° to 500° C. are particularly suitable for the promotion of the interaction of carbon monoxide and steam; according to German Patent 284,176 cerium compounds are also suitable; according to German Patent 293,585 mixtures of zinc oxide and chromium oxide are used. In German Patent 292,615 the preparation of catalysts of the iron group is described in detail. According to German Patent 297,258, porous earthenware, bauxite asbestos and other substances are soaked in 50 per cent. nickel nitrate solution and a previous purified mixture of water-gas and steam is passed over the resulting product at 500° to 600° C.

Moreover, according to German Patents 292,615, 293,943, 297,258 and 303,718 methane can be manufactured from carbon monoxide and steam with a nickel contact (see also Norwegian Patent 24,576 and Danish Patent 18,827). Nickel oxide or nickel also promote the action between hydrocarbons and steam at a dull red heat (German Patent 296,866). According to German Patent 300,032, a particularly effective catalyst is obtained, for example, by repeatedly etching small rolls of fine iron gauze with a concentrated solution of ferric nitrate and heating to a moderate temperature. Such a contact substance is extremely active at 500° C. Nickel cata-

[1] *Chem. Ztg.*, 1915, "Repertorium," p. 299.

lysts cause methane and carbon dioxide to react at high temperatures and concentrations according to the equation :

$$CH_4 + CO_2 = 2CO + 2H_2$$

(German Patent 306,301).

In German Patent 285,703 the B.A.S.F. describes a process of condensing carbon monoxide from water gas. In German Patent 282,505 the main features of the process of absorption by copper solutions are described. If the solutions which are used do not contain a definitely higher proportion of ammonia than 60 gm. in the form of free base or of carbonate, iron apparatus is not injured during working, even under pressure. The removal of the absorbed carbon monoxide is carried out during manufacture by reduced pressure. If the solution has become charged with cupric oxide by continual use, it is allowed to stand for some time before the carbon monoxide is removed ; the carbon monoxide then reduces the cupric oxide to the cuprous form. A suitable copper solution is obtained, for example, by mixing 200 kg. of cuprous chloride, 250 kg. of ammonium chloride, 500 kg. of 25 per cent. aqueous ammonia and 500 kg. of water. By working under pressures of 100 atm. and more, the smallest quantities of carbon monoxide are removed from hydrogen in an extremely short time. The ammonia which evaporates must be continuously replaced. According to German Patent 288,450, it is advisable to add small quantities of air to the gases or the absorbing liquid, on account of the separation of metallic copper which occasionally occurs. The apparatus is described with the aid of a sketch (Fig. 32) in German Patent 288,843. The cuprous solution passes continuously from the container, A, through the pump, B, into the absorption cylinder, C, into which the hydrogen containing carbon monoxide is introduced at D, and a little air at D'. The small quantity of air which is necessary for oxidation may also be introduced at E and removed at F. The hydrogen which escapes at G is free from carbon monoxide, and can be readily and completely freed from carbon dioxide by alkaline absorption or treatment with water under pressure. It is convenient to absorb the carbon monoxide under pressure, in which case a pressure-reducing valve must be provided between C and A. It is advisable to warm the copper solution to 30° to 60° C. Solutions of cuprous chloride gradually attack iron apparatus. The following solution is prefer-

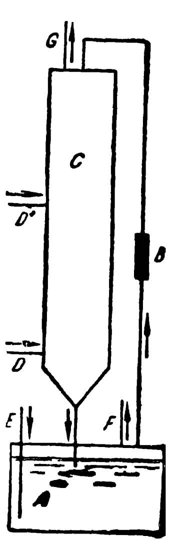

FIG. 32.

able: 40 parts of cuprous oxide are stirred with 100 parts of ammonium carbonate and aqueous ammonia with slight access of air (German Patent 289,694).[1]

Catalysts and contact masses are also dealt with in German Patents 312,726 and 313,192, and in French Patent 478,739.

The B.A.S.F. has evolved a special method for the complete removal of hydrogen sulphide from hydrogen and other gases which is protected by German Patents 302,555 and 303,292. The gases are first treated with suspensions of iron oxides or hydroxides in water or neutral salt solutions and then with alkaline suspensions, or suspensions of substances of alkaline reaction, or with solutions of such substances. The first washing liquor can be readily revivified by exposure to air. It is advisable to add to the solutions sufficient oxalic acid or acid potassium tartrate to almost, but not completely, dissolve the iron compounds. The B.A.S.F. produces considerable quantities of sulphur as a by-product of its gas purification processes.

The B.A.S.F. uses a very interesting method of determining traces of oxygen in hydrogen, which is described in German Patent 303,986. This consists in passing the gas under investigation over a catalyst and measuring the temperature rise caused by the combustion. The method also enables manufacturing processes to be controlled automatically. A similar process is described by R. Naumann in German Patent 313,858. The method of E. K. Rideal and H. S. Taylor [2] for the determination of very small traces of carbon monoxide also depends on physico-chemical methods. J. Soyer [3] determines small quantities (1 in 15,000 to 1 in 40,000) of hydrogen phosphide in hydrogen with accuracy by burning 2 to 20 litres of the gas in a platinum jet placed in a quartz tube, which is slightly inclined downwards, and the lower portion of which is cooled by a wet cloth; the phosphoric acid which is formed is collected in a little water and in two washing flasks.

On the manufacturing scale, apart from the Linde and the Linde-Frank-Caro processes, the B.A.S.F. uses producer gas which is mixed with water-gas and caused to react with steam in presence of a catalyst. The carbon monoxide of the producer gas and water gas then reacts according to the equation:—

$$CO + H_2O = CO_2 + H_2,$$

forming carbon dioxide, which is removed by absorption with water under pressure. By suitably adjusting the proportion of water gas the required mixture of one volume of nitrogen with three of hydrogen

[1] See also A. R. Lamb, *Chem. Zentralbl.*, 1920, iv., 640-641.

[2] *Chem. Zentralbl.*, 1919, iv., 521; see also J. J. Graham, *J. Soc. Chem. Ind.*, **38**, 10 (1919); *Chem. Zentralbl.*, 1920, iv., 661.

[3] *Chem. Zentralbl.*, 1919, iv., 311.

can be directly obtained. The residual carbon monoxide, which remains after the reaction with steam and removal of the carbon dioxide, is completely absorbed by ammoniacal cuprous oxide or other solutions. According to Haber[1] the B.A.S.F. attaches the greatest importance and value to this newest method of manufacturing hydrogen. C. Bosch[2] has described it in detail. Water gas and steam are caused to react in the presence of an iron or iron oxide catalyst at 400° to 500° C., with formation of a product containing 1 to 2 per cent. of carbon monoxide, together with carbon dioxide and hydrogen. The composition 1 to 3 is achieved by the addition of producer gas from which the carbon dioxide has previously to be removed by washing with water at 25 atm. pressure and then removing the last traces of carbon monoxide with cuprous oxide solution at 200 atm. pressure. This last absorption at high pressure is also necessary in the case of the Linde-Frank-Caro gas, which is produced in the large scale plant at Oppau. Electrolytic hydrogen cannot be used, as the cost of power is too high. Hydrogen obtained by the iron contact process is always too impure for direct use. The carbon dioxide, which is removed by absorption, is utilised for the production of ammonium sulphate by the gypsum process.[3] The new B.A.S.F. process of hydrogen manufacture is more economical for the purposes of ammonia synthesis than the methods which were utilised before its adoption, and these latter have therefore now become of subsidiary importance in the Badische works.

Attempts are also being made in other quarters to utilise the nitrogen in flue gases. In Austria the Kitzinger process of manufacturing nitrogen and carbon dioxide has been largely used. Flue gases, which contain an excess of oxygen, are cooled in a suitable chamber and are then passed through a series of purifiers in order to remove the dust. They then meet a current of producer gas in a heated retort filled with a porous contact material which leads to complete removal of the remaining oxygen. The escaping gaseous mixture mainly contains nitrogen, carbon dioxide and steam. The steam is condensed and the carbon dioxide is separated in an absorption tower. The nitrogen is sufficiently pure for direct use, traces of carbon dioxide being removed by treatment with lime.[4]

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Mixtures of nitrogen and hydrogen are produced from water gas. Pure nitrogen is also obtained from flue gases, but the most important

[1] "Aus Luft durch Kohle zum Stickstoffdunger" (Berlin, 1920), p. 22.
[2] *Chem. Ztg.*, 1920, p. 721.
[3] "Aus Luft durch Kohle zum Stickstoffdunger," p. 22.
[4] See the similar method of N. Caro and German Patent 324,868.

source is the fractionation of liquid air (German Patents 324,266, 324,661, 327,127, 329,361; U.S. Patents 1,415,058, 1,420,625; and British Patent 146,397/1920). The liquefaction of air is dealt with in *Zeitsch. f. angew Chem.* (1923), 262; its rectification in German Patents 324,083, 329,542, 332,548, 336.719, 340,509; see also F. E. Norton, *Chem. and Met. Eng.*, **23** (1920), 511. The storage and transport of liquid air is dealt with in German Patents 307,736, 320,781, 324,261, 324,661/2, 326,904, 330,940, 336,092, 337,400, 337,736, 350,839; and its use for the production of explosives in German Patents 300,728, 304,300, 306,450, 325,857, 333,895, 347,671, 348,137, 350,479; see also *Chem. Ztg.* (1922), 532. Liquid air or liquid oxygen is also used as an addition to the blast in blast furnaces (*Stahl u. Eisen*, 1922, **47**, 456) and as an accelerator in the oxidation of ammonia (German Patent 304,823), as a supply for rescue apparatus (British Patent 174,418/1922; *Chem. Ztg.* (1921), 117, 142), and for cooling nitrous gases (German Patents 289,846 and 304,372).

Nitrogen is obtained by chemical methods, more particularly from flue gases, according to Austrian Patent 82,747; French Patent 519,132; German Patents 322,995, 337,942, 323,974.

Ozone is obtained by the silent electric discharge (German Patents 336,943, 347,413; *Chem. Ztg.* (1922), 747, 909), and is used for the ozonisation of materials (Norwegian Patent 31,439), of the products of sugar manufacture, ethylene (German Patent 334,615), the rapid seasoning of wood and the oxidation of petroleum products. Helium and argon are dealt with in German Patents 340,987 and 353,743. The residual gases from the synthesis of ammonia, containing 70·6 per cent. H_2, 23·5 per cent. N_2 and 5·9 per cent. of argon, can be used for the isolation of the latter gas.

Production of Hydrogen. This material can be obtained: (*a*) By the action of steam on iron (German Patents 303,952, 328,691, 330,467, 330,644, 330,800, 332,111, 332,891, 337,153, 337,794; British Patents 147,235/1918, 175,501/1920; French Patents 534,950/1 536,816/8; Austrian Patents 88,373/6; Swiss Patent 91,856).

(*b*) By electrolysis (*Seifensieder Ztg.* (1921), **48**, 1003—removal of CO; German Patents 341,149, 341,153, 335,992, 351,383, 329,361; *Chem. Ztg.* (1921), 74, 94; British Patent 171,743/20; French Patent 524,468). The latter patents describe the utilisation of the pressure of the cathodic hydrogen.

(*c*) Production from water gas by chemical removal of the carbon monoxide, is described in German Patent 303,931; French Patent 535,105; U.S. Patents 1,424,749, 1,428,879. Its removal by partial liquefaction by the methods of Linde-Frank-Caro, Claude, etc., is described in German Patent 339,490; Swiss Patent 92,976; ***Zeitsch.***

kompr. u. flüssige Gase, **22**, 77 (1922); *Compt. rend.*, **172**, 974 (1921); **173**, 653 (1922); *Jour. Ind. Eng. Chem.* (1922), **14**, 1118; see also French Patent 535,296.

(*d*) By decomposition of hydrocarbons (U.S. Patents 1,363,488, 1,418,385; French Patent 535,105; German Patents 328,637, 343,391).

(*e*) Its production from steam and sulphur is described in British Patents 176,779/1922, 181,326/1922; German Patent 352,186.

(*f*) From alloys, hydrides, iron and acids (U.S. Patent 1,366,185; German Patents 303,281, 311, 987, 346,119).

The purification of hydrogen is described in German Patents 329,177, 357,135. The gas is used for the synthesis of ammonia, in aeronautics, for fat hardening (see *inter alia*, German Patent 341,189; British Patent 140,371/1920; *Chem. Ztg.* (1921), 27, 125); for hydrogenating naphthalene (*Chem. Ztg.* (1921), 565); for hydrogenating coal (Bergius and others, German Patents 299,783, 303,272, 303,332, 306,356, 307,671); for the production of artificial gems in the oxy-hydrogen blow pipe (German Patent 332,390; *Chem. Ztg.* (1922), 219); for autogenous welding (British Patent 158,633/1919). The synthetic production of organic substances, for example, from acetone and hydrocarbons (German Patents 347,610, 349,089), and from carbon monoxide and hydrogen (British Patent 180,016/1922), is of rapidly increasing importance. There are articles of general interest in *J. Soc. Chem. Ind.*, **41**, 168 (1922); and *Journal f. Gasbeleuchtung*, **63**, 91, 92.

CHAPTER XXIII

Older Methods of Manufacture of Nitric Acid from Nitrate[1]

WE are justified in a short consideration of the manufacture of nitric acid from nitrate and sulphuric acid, which has been described in detail by Lunge [2] and others, not only for historic reasons, but also because nitrates produced from atmospheric nitrogen were utilised during the War for the production of concentrated nitric acid in this manner on account of the absence of any other suitable method of concentration.

Until about forty years ago only two qualities of nitric acid were manufactured—namely, the ordinary acid of 55 to 65 per cent. strength and 1·35 to 1·40 specific gravity and the stronger, red fuming acid. The most marketable quality to-day is an acid containing 92 to 95 per cent. HNO_3, of specific gravity 1·5 to 1·52, the manufacture of which involves many difficulties, as strong acid easily decomposes according to the equation—

$$2HNO_3 = N_2O_3 + O_2 + H_2O.$$

100 per cent. nitric acid is only stable at atmospheric pressure below 0° C. It commences to boil at 86° C. with decomposition, causing dilution and red coloration by nitrogen oxides. At 120° C. and atmospheric pressure an acid distils containing 35 per cent. water and of 1·4 specific gravity.

Formerly cast-iron retorts were almost universally used, which were connected with a series of earthenware coolers and condensers and a final scrubbing tower. For the manufacture of acid of 1·35 to 1·4 specific gravity the retorts were charged with Glover acid of 60° Bé. or with sulphuric acid of 66° Bé. if the more concentrated product was to be obtained. Chile nitrate of 95 to 96 per cent. quality is decomposed mainly below 160°, smoothly and quickly, according to the equation—

$$NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4.$$

The Übel retort of the Rhenania Company and the five-pan system of the B.A.S.F. have proved entirely successful in practice.

All the above-mentioned methods are inferior in quality of product, yield and economy to Valentiner's method of vacuum distilla-

[1] See Ost, "Lehrbuch der Chemischen Technologie" (Leipzig, 1919), 10th edition, pp. 162 et seq.

[2] "Handbuch der Schwefelsäurefabrikation." vol. i. (1916), pp. 138 et seq.

tion, which, now that serious practical difficulties have been overcome, has been converted into a very reliable process during the last few years. By this process a vacuum is produced in the cast-iron retorts in order to effect a smoother distillation. In the Valentiner retort, under the influence of the vacuum, a "crisis" occurs at 120° C.—that is, a very sudden and correspondingly energetic decomposition of the charge, which was previously quiescent. In order to avoid all danger, the retorts are therefore provided with a safety valve in the cover.

In the Valentiner process the yield of 96 to 100 per cent. acid may amount to 80 per cent. The charge of a normal retort is 1,000 kg. sodium nitrate, 1,000 kg. sulphuric acid of 66° Bé., and so much dilute nitric acid as contains 100 kg. of water. The distillation lasts about 10 hours and the vacuum in the retort is maintained at 30 mm. of mercury, but care is taken that a little air is continuously drawn into the retort ; this is important in order to ensure steady distillation and to decolorise the distillate.

The main reaction occurs at about 120° C., and the "crisis," which lasts for one hour, occurs at 120° to 130° C. ; the temperature then drops slowly and is then raised to 175° by external heating, and finally to 210°, at which temperature the sodium bisulphate can be drawn off in a perfectly fluid condition.

The effective condensation of the distilled acid by tourilles and coolers is important ; if, for example, 12 tourilles are used the acid is distributed more or less as follows :—

1 and 2 (originally empty) : Main yield, of about 600 kg., 95 to 96 per cent. nitric acid.
3 to 5 (originally empty) . 200 kg. acid of about 100 per cent. concentration.
6 (charged with 40 kg. of 20 per cent. acid) : 90 kg. of acid of approximately 70 per cent.
7 (charged with water) : 50 to 54 kg. of acid of about 30 per cent.
8 and 9 (empty) : Condensates.
10 (charged with water) : 10 per cent. acid.
11 and 12 (charged with milk of lime) : By-product fertiliser.

The charges 11 and 12 also serve to protect the vacuum pump from the acid spray and vapours. Wet air pumps with rubber valves are ordinarily used. The escaping gases always contain a very small amount of nitrous compounds.

Aldo Chiappero gives a general description of a Valentiner plant in *L'Ind. chimica*, **6**, 41 (1919) which includes a summary of yields

and concentrations. We may also refer to the annual reports of K. Reusch[1] and articles[2] by J. Grossmann, E. J. Pranke, H. P. Basselt, L. Mauge and H. J. Paoli, and, finally, German Patents 281,211, 283,212, 300,712, 301,702, 303,557 ; French Patent 462,290 ; and British Patents 110,637/1916 and 127,677/1917.

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Details of modern methods of decomposing nitrate by sulphuric acid, etc., are to be found in German Pats. 301,702, 348,288, 307,601, 337,183; Austrian Pat. 87,470; U.S. Pat. 1,415,395; French Pats. 538,201, 538,863; British Pat. 166,557/20. Comparisons of costs are given in *Chem. Age*, **7**, 115, 200, (1922).

[1] *Chem. Ztg.*, 1919, pp. 542, etc. ; see also *Chem. Zentralbl.*, 1920, iv., 739–740.

[2] *J. Soc. Chem. Ind.*, **35**, 155 (1916) ; **36**, 1035 (1917) : *Chem. Zentralbl.*, 1919, ii., 491, 659, 743 ; 1920, ii., 799 , *Chem. Ztg.*, 1920, *Chem. Techn. Übers*, p. 189.

CHAPTER XXIV

The Arc Synthesis of Nitric Acid

THE excellent summary of Wilh. Moldenhauer [1] on the reactions of free nitrogen renders it unnecessary to enter here into the details of the history of this process and of the scientific work connected with the important synthesis of nitrogen oxides from the nitrogen and oxygen of the air. It will suffice to refer to the most important work mentioned by Moldenhauer.

In 1781 Cavendish observed the occurrence of compounds of nitrogen and oxygen on burning hydrogen in air, and thus effected the first synthesis of nitric acid. A few years later, in 1784, he carried out the first electric synthesis by passing sparks from an electric induction machine through air. All later work depends on these two foundations.

Muthmann and Hofer [2] were the first who attempted to follow the exact equilibrium of the reaction

$$N_2 + O_2 \rightleftarrows 2NO$$

They caused an alternate current arc of 2,000 to 4,000 volts to burn in a glass flask, and endeavoured to determine the temperature by determining the decomposition of carbon dioxide into CO + O under the same conditions, as exact measurements of le Chatelier were available for the latter reaction. This method of measurement was, however, too crude to give really satisfactory values. The practical figures which Muthmann and Hofer found are more important. The concentrations fluctuated from 3·6 to 6·7 per cent. of NO by volume, and the energy required was found to be 7·71 k.w.h. for 477 gm. NO or 1 kg. HNO_3.

Nernst [3] carried out further measurements on the nitric oxide equilibrium. He passed dry atmospheric air through an iridium tube which was electrically heated to a very high temperature. The nitric oxide which was formed was rapidly removed from the heating zone of the reaction tube by means of a quartz capillary cemented to the same, so that there was little danger of decomposition of the product. Nernst found that the most reliable values were :—

0·64 per cent. NO by volume at 2,033° abs.

0·97 per cent. of air by volume at 2,195° abs.

[1] *Ber.* 1920, pp. 154 *et seq.*

[2] *Ibid.* 1903, p. 438.

[3] "Reports of the Kgl. Ges. d. Wissensch. Göttingen," 1904, p. 261 ; *Zeitsch. f. anorg. Chem.*, 49, 213 (1906) ; *Zeitsch. f. Elektrochem.*, 12, 527 (1906).

and from these results he calculated the following equation with the help of the reaction-isochore

$$\frac{d \log k}{d\mathrm{T}} = -\frac{q}{\mathrm{K}.\mathrm{T}^2},$$

in which k represents the expression

$$\frac{[\mathrm{NO}]^2}{[\mathrm{N_2}].[\mathrm{O_2}]} = \frac{x^2}{\left(79{\cdot}2 - \frac{x}{2}\right)\left(20{\cdot}8 - \frac{x}{2}\right)},$$

and x is the percentage concentration of NO by volume. From this equation he found that the heat of formation of nitric oxide was $q =$ — 45,600 cals., which is in good agreement with the value of — 43,200 cals. found by Thomsen by direct thermo-chemical measurement. Greater accuracy was achieved by further experiments of Nernst, which were fully confirmed by Jellinek.[1] In these further experiments the reaction chamber consisted of a platinum vessel shaped like a pipette, which was enclosed in a massive electrically heated platinum furnace. On passing air through the apparatus, appreciable quantities of nitric oxide were found below 1,500° C., but the quantity could not be determined with certainty. However, by comparing the velocities of formation and decomposition, a reliable value of the equilibrium constant was found for the bi-molecular reaction:—

$$\mathrm{N_2} + \mathrm{O_2} \rightleftarrows 2\mathrm{NO}.$$

At a temperature of 1,811° abs., a concentration of 0·37 per cent. NO by volume was found, whilst Jellinek, who carried out larger experiments at the instigation of Nernst, found 0·42 per cent. by volume at 1,877° abs.

Finkh[2] investigated the amounts of nitric oxide formed during the explosion of detonating gas mixed with air, and Nernst used his figures as a foundation in order to calculate the nitric oxide equilibria at higher temperatures from the above equations. The equilibrium values so obtained were 2·05 per cent. of NO by volume at 2,850° abs., and 2·23 per cent. at 2,675° abs. The following table shows how well the values found in the iridium furnace at 2,195° abs. agree with those calculated from the heat of formation of — 43,200 cals. found by Thomsen and the reaction-isochore:—

Temperature T in absolute degrees.	Nitric Oxide Equilibrium x (Observed).	Concentrations x (Calculated).
1,811°	0·37	0·35
1,877°	0·42	0·43
2,033°	0·64	0·67
2,195°	0·97	0·98
2,580°	2·05	2·02
2,675°	2·23	2·35

[1] *Zeitsch. f. anorg. Chem.*, **49**, 229 (1906).
[2] *Ibid.*, **45**, 116, 126 (1905); see also E. Rasch, *Elektrotechn. Zeitsch.*, 1901.

At a later date Pollitzer [1] revised these figures, using Nernst's thermal equation.

By extrapolation of Nernst's results up to a concentration of 7 per cent. of NO by volume, a temperature of 3,750° is found, corresponding to the assumed temperature of the electric arc. This value agrees with the practical results obtained by Muthmann and Hofer, Brode, MacDougall and Howles, who obtained 6·7 to 7·4 per cent. of NO by volume in the electrically treated gases.[2] It was therefore generally assumed that the formation of nitric oxide was a purely thermal reaction. This view was supported by further investigations[2] of Grau and Russ and of Le Blanc and Niiranen.

Haber and Koenig [3] then discovered conditions under which a specific electric action of the arc must be assumed.[4] Brode had observed that the nitric oxide concentration increases if the arc is cooled. Haber and Koenig started from this result, which had at that time not been correctly explained. They produced a relatively cold alternate current arc by working at a reduced pressure of 100 mm. of mercury only, burning a widened arc in a narrow tube of glass or quartz, which was cooled with water; they then slowly passed a current of mixed nitrogen and oxygen along the tube. They thus obtained the following results :-

Gaseous Mixture.		NO.	Absolute Temperature T calculated by Nernst's Thermodynamic Equation.
Per cent. by Volume of O_2.	Per cent. by Volume of N_2.	Per cent by Volume	
20·9	79·1	9·80	4,334°
48·9	51·1	14·40	4,650°
44·4	55·6	14·30	4,650°
75·0	25·0	12·77	4,767°
81·7	18·3	12·10	5,000°

By introducing into the body of the arc an extremely fine platinum wire of 0·01 mm. diameter it was proved that temperatures may have occurred which exceeded the melting point of platinum by a couple of hundred degrees, but which certainly did not attain the calculated figure; a certain direct action of the electric discharge was thus proved. As the same equilibrium values for the proportion of nitric oxide were obtained when nitric oxide itself was exposed to the arc

[1] See Nernst, "Die theoret u. experim. Grundlagen des neuen Wärmesatzes" (Halle, 1918), p. 118.

[2] See Moldenhauer, *loc. cit.*, pp. 159–160.

[3] *Zeitsch. f. Elektrochem.*, **13**, 725 (1907); **14**, 689 (1908).

[4] *Ibid.*, **11**, 752 (1905).

under the same conditions, Haber and Koenig coined the expression "electric equilibrium." This differs from the thermal equilibrium by the fact that a definite amount of electrc energy per unit of time is necessary, the value of which is a measure of the deviation from the thermal equilibrium. The following calculations, in which k_e = electric equilibrium and k_t = thermal equilibrium, represent the relation between the two equilibrium constants, as the ionic impact is more favourable to the formation than to the decomposition of NO:—

$$k_e = \frac{[NO']}{[N_2']^{\frac{1}{2}}[O_2']^{\frac{1}{2}}} \text{ and } k_t = \frac{[NO]}{[N_2]^{\frac{1}{2}}[O_2]^{\frac{1}{2}}}.$$

The ratio of k_e to k_t depends on the velocity with which the thermal decomposition occurs at the temperature in question. With diminution of the temperature of the arc, k_e differs increasingly from k_t. In a cooled direct current arc Morden, Holwech and Koenig later found concentrations up to 9 per cent. NO.

Numerous investigators observed that the synthesis of nitric oxide can be accelerated by the choice of suitable catalysts, such as platinum, iridium and iron.[1] The formation of nitrogen oxides during the slow oxidation of phosphorus in air was already known to Schönbein in 1849.[1] Considerable work has been carried out on the production of nitrogen oxides together with ozone by the dark electric discharge.[1] There are also a number of communications on methods of activating oxygen or nitrogen electrically and so rendering them more reactive. After Strutt's[1] experiments with activated nitrogen had been unsuccessful, Fr. Fischer and E. Hene[2] achieved a series of better results. As a result of their experiments, they came to the conclusion that the formation of nitric oxide in the high-tension arc was preceded by activation of the oxygen and not of the nitrogen. According to Koenig and Elöd, however, both components are activated.[3] The experiments of E. Müller[4] on nitric oxide formation in a high-tension arc deflected by an air current are interesting. M. Novak[5] supplies a communication on the oxidation process of D. Helbig (German Patent 225,239), who obtained 1 to 1·5 per cent. of NO in a similarly constructed 250-k.w. furnace. The absorption of these dilute gases was very satisfactory and attained 90 to 96 per cent. of the theoretical.

[1] See Moldenhauer, *loc. cit.*, pp. 162 *et seq.*

[2] Dissertation of E. Hene (Berlin, 1912); Fischer and Hene, *Ber.*, **45**, 3652 (1912); **46**, 603, 4103 (1913).

[3] *Ber.*, **47**, 516 (1914); see also E. Elöd, "Dissertation" (*Chem. Ztg.*, 1916, "Repert.," p. 6) (Karlsruhe, 1915).

[4] E. Müller, "Versuche über die Stickoxydbildung aus Luft im zerblasenen Hochspannungslichtbogen" (Ak. Heidelberg, 1918).

[5] *Chem. Ztg.*, 1919, pp. 52, 95.

With regard to more general technical communications, we must refer to various periodical reports.[1] F. Gros carried out successful experiments to raise the yield of nitric acid, which had then attained a figure, according to him, of 55 to 65 gm. of HNO_3 per kilowatt hour in large industrial installations. In experimental installations which exceeded the ordinary laboratory dimensions, he succeeded in obtaining 90 gm. HNO_3 per kilowatt hour by using a dry mixture of 50 per cent. N_2 and 50 per cent. O_2 and recovering the nitrous gases by refrigeration.[2]

Interesting data on the early days of the atmospheric nitric acid industry are given more particularly by K. W. Jurisch[3] and A. Neuburger.[4] The first suggestion for the technical utilisation of Cavendish's reaction was made by a lady, Mme. Lefebre, of Paris, who, much in advance of her time, applied for British Patent 1,045 on "The Manufacture of Nitric Acid" in 1859. Her apparatus was similar to that used by Muthmann and Hofer. Mme. Lefebre already recognised the advantage of an admixture of oxygen, which was produced electrolytically. Her patent specification includes a plan of a manufacturing installation, although such an installation would naturally have had very little hope of success, considering the low state of development of electro-technology at that time. As a matter of fact, her process was never carried out on a large scale.

The work of Crookes in 1892,[5] and Lord Rayleigh in 1897, was followed in 1899 by MacDougall's British Patent 4,643/1899, Austrian Patent 2,805, and Swiss Patent 20,092; he was the first to utilise the arc on a considerable scale. MacDougall used a dynamo and transformer, together with compressed air enriched with oxygen. At a later date he used alternate-current machines capable of supplying current at a periodicity of 50 and at 7,500 volts. He used 500 units, in which the electrodes were 50 mm. apart. The yield was 25 gm. of HNO_3 per horse power hour.[6]

The first process to be operated industrially, at least for a short interval, was that of C. S. Bradley and R. Lovejoy,[5] who founded the Atmospheric Products Company of Jersey City, N.J., in 1902, with a capital of one million dollars. Their process is described in British Patent 8,230/1901, U.S. Patents 709,867, and 709,869, Austrian

[1] *Chem. Ztg.*, 1913, No. 110 *et seq.*; 1915, No. 118 *et seq.*; 1920, pp. 625 *et seq.*, pp. 794 *et seq.*; 1916, pp. 873 *et seq.*; 1919, p. 403; 1920, pp. 873 *et seq.*, *Chem Ind.*, 1919, Nos. 22–23. See also *Chem. Zentralbl.*, 1919, **2**, 338, 741; **4**, 533, 777; 1920, **4**, 388, 430; **2**, 485; **4**, 38, 603.

[2] *Compt. rend.*, **170**, 811 (1920).

[3] "Salpeter and sein Ersatz" (Leipzig, 1908).

[4] *Zeitsch. f. angew. Chem.*, 1905, p. 1850; *Chem. Ztg.*, 1913, "Repert." p. 365.

[5] See O. N. Witt, *Chem. Ind.*, 1905, p. 703.

[6] *Zeitsch. f. angew. Chem.*, 1903, p. 1717.

Patent 12,300, and Swiss Patent 24,298. The inventors use high-tension direct current, which is frequently interrupted by mechanical arrangements. A steel shaft, driven electrically, and making 500 revolutions per minute, is passed through a hollow vertical iron cylinder, 1·5 m. in height and 1·25 m. in diameter. On to the shaft there are keyed 23 brass sleeves, each of which carries 6 radially arranged rods of brass and platinum ; the same number of counter-electrodes are attached to the wall of the drum. On closing the circuit an arc is produced between each two corresponding poles, which is stretched to a length of 100 to 150 mm. before breaking on account of the rapid revolution of the shaft. Another arc is then produced and the cycle thus goes on continuously. The first installation of this kind[1] contained 185 arc contacts, and each arc was formed and broken 50 times per second. With a current of 0·75 amp. at 8,000 volts, the number of arcs per second was 6,900, and each arc consumed 1 milliamp. After being first dried with calcium chloride and pre-heated, air passed into the apparatus, whilst the reaction gases were carried into an iron reservoir and then into an absorption tower, in which the nitrogen oxides were absorbed by water or caustic soda solution. One kilogram of nitric acid was obtained per 15·4 h.p. hours. The final products, nitric acid and nitrates, always contained nitrous acid or nitrites. These impurities could not be removed economically, and the products had therefore to be sold in an impure condition. This fact considerably reduced the uses for which they were available. The installations were, moreover, complicated and unreliable, in view of the relatively small output, and could not therefore be operated profitably for long. After the appearance of the Schönherr process only one installation remained at work.[2] The Atmospheric Products Company therefore ceased to operate after 1904. The final yield of nitric acid was better than in the earlier experiments, but the furnaces were only able to treat 19·5 cu. m. of air per hour.[3] Among various later patents we may mention U.S. Patents 829,874, 829,876, 904,070, and German Patent 179,288.

The first definite success along these lines was achieved by the Norwegians, Chr. Birkeland and S. Eyde, in 1903, after the project of the Freiburg physicist, Kowalski, and his co-worker Moscicki, who proposed to utilise alternating current at 50,000 volts. (U.S. Patent 754,147), had failed. It was already known before Birkeland's investigations that the alternate-current arc could be distorted into disc form by magnetic action, but it was not known that these dis-

[1] *Zeitsch. f. angew. Chem.*, 1904, p. 1713.
[2] *Elektrotechn. Zeitsch.*, 1909, Parts 16–17.
[3] *Zeitsch. f. angew. Chem.*, 1906, pp. 37–38, 977.

torted arcs produced an exceptional quantity of nitric acid in the surrounding air. The constructive development of the Birkeland disc arc into an economic air-combustion furnace is due to S. Eyde and his co-workers. The first patents—namely, British Patent 20,003/1904; French Patent 335,692; Norwegian Patents 12,879, 12,961, 12,989, 13,240, 13,280, 13,281, 13,415, 13,507, 13,705, 13,738, 13,753, 17,302, 17,352, 17,839; Swiss Patent 29,711; U.S. Patents 772,862 and 775,123—contain the essential features of the process,[1] which has been described in detail by O. N. Witt, Edström, Neuburger, and the inventors.[2]

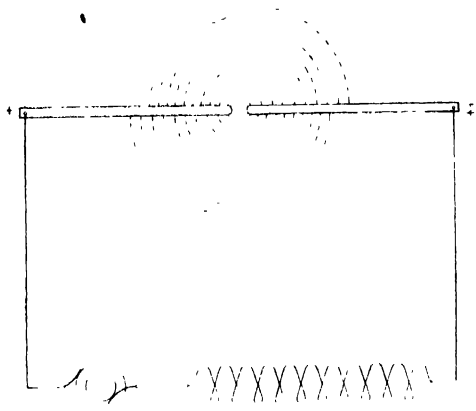


FIG. 33.—Diagrammatic representation of alternate current arc, magnetised by direct current.

The forces acting in the magnetic field exert a constant tendency to extinguish the alternate current arcs. For this reason, instead of a single arc flame, a series of oscillating flames is formed in the two directions, and these flames fluctuate up and down with a velocity of 100 m. per second, so that the general impression is obtained of a continuously burning disc of electric flame two or more metres in diameter (Fig. 33). These disc arcs are enclosed in flat fireclay furnaces armoured with copper, through which a powerful air current is blown. The furnace is built between the poles of a powerful direct-current electromagnet. The electrodes form what may be described as a cross

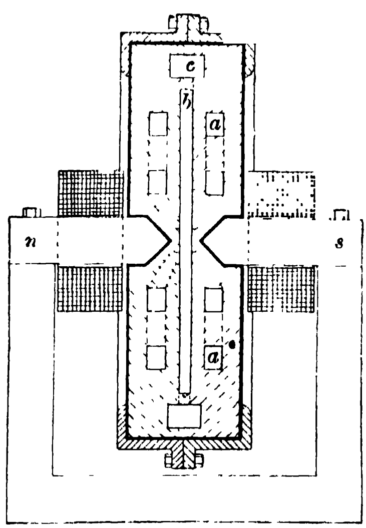


FIG. 34. Diagrammatic representation of Birkeland-Eyde arc furnace. Original form.

[1] *Chem. Ztg.*, 1904, p. 997; *Elektrochem. Zeitsch.*, **11**, 143 (1904): *Elektrotechn. Zeitsch.*, 1904, p. 1043; *Elektrochem. Ind.*, **2**, 399 (1904); see also Ullmann's "Encyclopædia," vol. ix., (1921), pp. 635 *et seq.*

[2] *Chem. Ind.*, 1905, pp. 699 *et seq.*; *Chem. Ztg.*, 1905, p. 1261. *Zeitsch. f. angew. Chem.*, 1905, pp. 217, 1761; 1906, pp. 37, 38, 983, 984. *Zeitsch. f. Elektrochem.*, **12**, 33 (1902).

with the two armatures of the electro-magnet at such a distance that a short circuit would immediately occur were it not for the dispersing effect of the magnet. The hollow copper electrodes are cooled internally by water and have a comparatively long life.

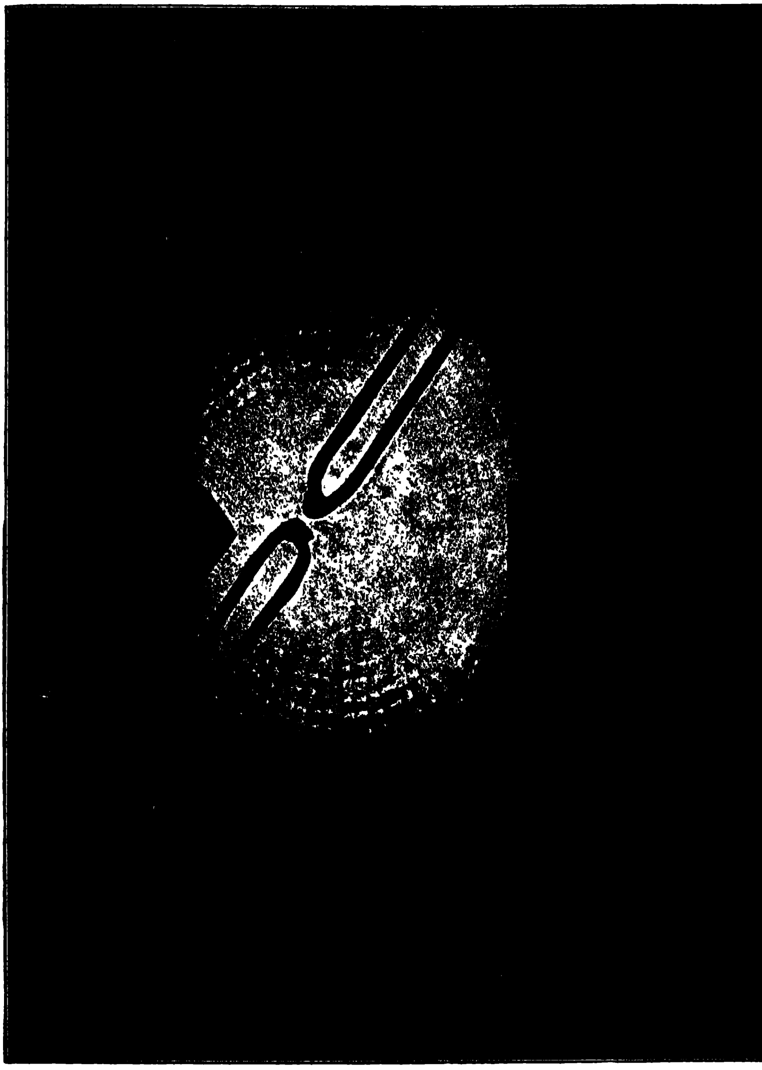


FIG. 35.—Photograph of alternating arc flame.

Air passes through the channels *a* within the fireclay walls of the furnace (Fig. 34) and then enters the arc chamber *b*. The oxidised out-going gases leave the furnace through *c*, at which stage they are brown in colour, owing to the presence of 1 to 2 per cent. of NO. The fireclay linings of these furnaces last for months, whilst the copper

electrodes, which are 1·5 cm. in diameter, must be changed on an average every six weeks. Fig. 35 is a photograph of the alternating high-tension arc.

"In a later type of this furnace [1] the space relations were somewhat altered without any alteration in fundamental principle. The magnets are box-shaped. This enables the construction of the furnace to be distinctly more convenient, and it is suspended from a frame of powerful iron pillars as a heavy structure which, however, may almost be called beautiful" (Fig. 36).

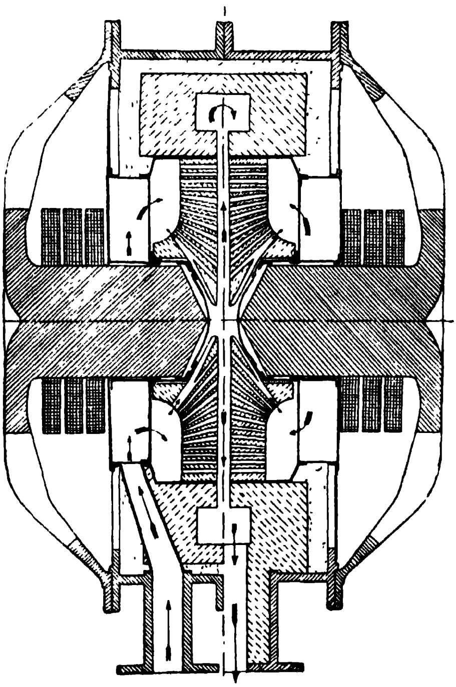


FIG. 36. Diagrammatic representation of Birkeland-Eyde arc furnace. Newer form.

In 1903 the suitability of the process for large-scale manufacture was demonstrated in a laboratory furnace of 3 h.p. In the same year the Norwegian Electric Company (Norwegische Elektrische Aktiengesellschaft) erected larger furnaces of 10 to 20 h.p. at Ankerlökken, near Christiania. The furnace gases were utilised industrially. The furnaces utilised 75, 200 and 500 kw. and were supplied with alternate current of a periodicity of 50 at 5,000 volts. The favourable result of these experiments and the insufficient electric supply from the town of Christiania led to the erection of a larger experimental plant at Vasmoen, near Arendal. At the same time plans were prepared for the first large works at Notodden, in Telemarken, of which O. N. Witt,[2] writes as follows: "The watercourses of the Hitterdal expand at Notodden to form a lake, which is connected by a series of navigable watercourses with the Skien Fjord and thus with the open sea, so that cheap water transport for the products is available. Close to Notodden the large Tin-Elf forms the Tinfos of 20,000 potential h.p. of which a part was developed to start with. Four kilometres above this fall the

[1] O. N. Witt, *loc. cit.*, p. 704.
[2] *Loc. cit*, p 705.

Tin-Elf forms the Svaelgfos." On May 2nd, 1905, the Norsk Hydroelektrisk Kvaelstof Aktieselskab started operations at Notodden.

The original installation comprised three Birkeland-Eyde furnaces of 500 to 600 kw., treating 75 cu. m. of air per minute. The disc arcs were of about 1·8 m. diameter. The gases may only be exposed to the high temperature of the arc for a very short period; they must very rapidly be removed from the reaction zone and cooled, as otherwise the reversibility of the reaction causes the complete decomposition of the nitric oxide which is formed. On the average the reaction gases contain 1 to 2 per cent. of NO. It is obvious that the absorption of such dilute nitrous gases must be a matter of serious difficulty, and in actual fact much work was necessary before suitable arrangements were devised. At Notodden the hot gases are first utilised for heating steam boilers for the evaporating pans and so on.[1] They then pass into aluminium coolers, where they are finally cooled to the ordinary temperature and then passed to the absorption towers. They are here converted into NO_2 by the atmospheric oxygen, which is, of course, present in excess:—

$$2NO + O_2 = 2NO_2.$$

On reduction of the speed of the air current, the oxidation, which has already started in the coolers, proceeds smoothly. At first enamelled sheet-iron tanks were used as oxidising chambers, but were later replaced by much more suitable empty absorption towers of acid-proof masonry. By means of a stoneware fan the NO_2 gases are then passed through a system of absorption towers of granite, stoneware, and so on, which are filled with quartz fragments and down which water trickles at a uniform rate. The acid which escapes below is circulated through the towers by pressure pots until an average concentration of 50 per cent. is obtained. Eight absorption towers suffice for the three furnaces at Notodden. The gases are then passed into two wooden towers fed with milk of lime, and finally into a chamber charged with solid lime. In the former solutions are formed which contain much calcium nitrite. At Notodden these liquors were originally treated with tower acid and the nitrogen oxides which were evolved were returned to the absorption towers.

The pure acid was originally completely neutralised with limestone. The calcium nitrate solution so obtained was mixed with the effluents from the two lime towers, evaporated and filled into iron drums in a molten condition, forming the well-known calcium

[1] *Chem. Zentralbl.*, 1920, iv., 79.

nitrate or Norway nitrate. J. Laudin [1] gives the following analysis of this product :—

$Ca(NO_3)_2 + 4H_2O$. Theoretically 11·86 per cent. N, actually 11·28 per cent.

Insoluble : 0·01 per cent. Traces of Fe_2O_3, Al_2O_3, and MgO.

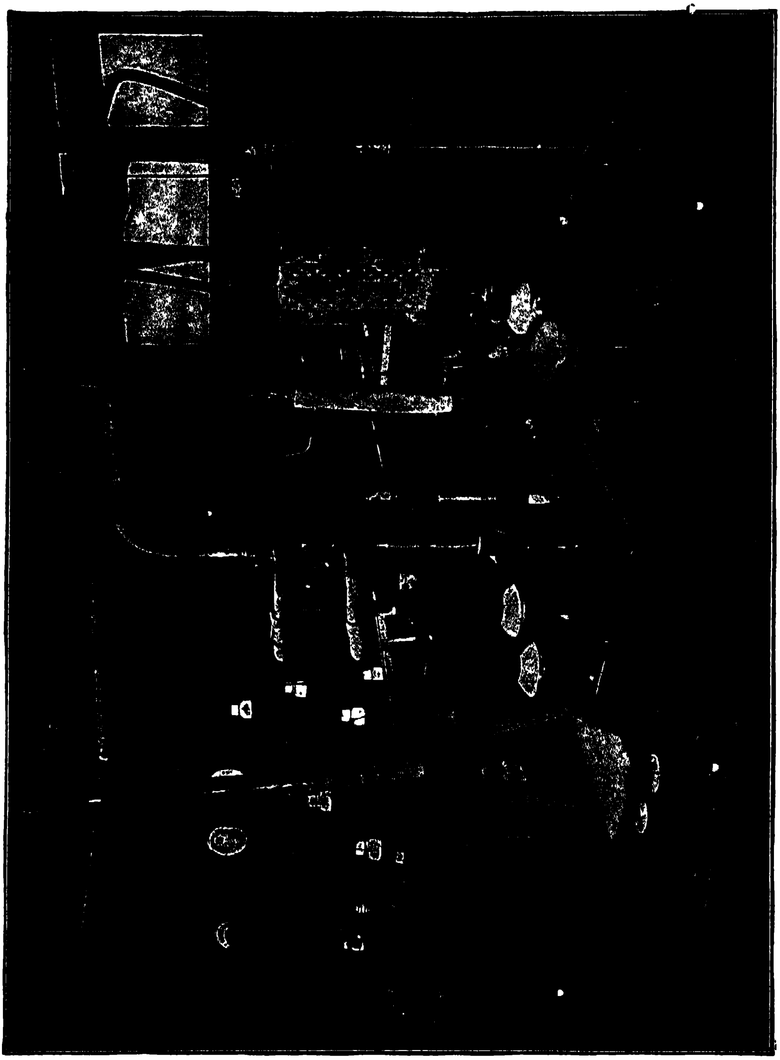


FIG. 37.—Experimental Birkeland-Eyde plant.

The Notodden plant, which is depicted in Figs. 37 to 42, comprised three furnaces in 1905, of a total current consumption of 1,500 kw., which, when fully utilised, produced 1,500 kg. of HNO_3 daily, or the corresponding quantity of nitrates. The average

[1] *Tekn. Tidskrift*, **22**. 10 (1904) ; *Zeitsch. f. angew. Chem.*. 1905, p. 264.

cost of electric power in southern Norway at that time, according to O. N. Witt, could be taken as 12*s*. per horse-power year.[1]

As already mentioned, the formation of nitric oxide in the high-tension arc takes place according to the following thermo-chemical equation :—

$$N_2 + O_2 = 2NO - 43{\cdot}2 \text{ cals.}$$

According to Ph. A. Guye and Nernst,[2] the following time intervals are necessary in order to establish the nitric oxide equilibrium :—

At 1,500° C.	1¼ days.
,, 2,100° ,, ...	5 seconds.
,, 2,500° ,, ...	0·01 seconds.
,, 2,900° ,, ...	0·000,035 seconds.

Decomposition, according to the equation

$$2NO = N_2 + O_2 + 43{\cdot}2 \text{ cal.},$$

commences to be appreciable at 700° C.; at 1,600° C. it is very rapid and is considerably accelerated by the electric spark or by a red-hot iron wire. The rapid cooling of the hot gases from the arc should extend to below 1,000° C., as below this temperature only is the NO practically inert and "frozen equilibrium" is attained.

In order to comprehend the absorption phenomena which will be considered later, it is necessary to realise the property of nitric oxide, which is colourless, of reacting with elementary oxygen, such as is present in the air in the oxidising chambers, at temperatures below + 150° C., with formation of reddish-brown nitrogen dioxide, according to the equation

$$2NO + O_2 = 2NO_2.$$

This reaction is important, both in this case and in that of the absorption of the gases which are obtained by the oxidation of ammonia. As this reaction takes place with evolution of heat to the amount of 27 calories, the formation of nitrogen dioxide should be assisted by the removal of as much heat as possible. At temperatures above 150° C. nitrogen dioxide dissociates into nitric oxide and oxygen, and dissociation into these components is complete at 620° C.[3]

The interaction of nitrogen dioxide gas with water is commonly assumed to take place according to the following equations :—

$$3NO_2 + H_2O = 2HNO_3 + NO, \text{ and}$$
$$2NO_2 + H_2O = HNO_3 + HNO_2.$$

[1] *Loc. cit.*, p. 705.
[2] K. A. Hoffmann, "Lehrbuch der anorganische Chemie" (Brunswick, 1919), 2nd edition, pp. 114–115, 123.
[3] *Loc. cit.*, pp. 114–115, 123.

In the first instance we will ignore the part played by the equilibrium condition :—

$$NO + NO_2 \rightleftarrows N_2O_3.$$

The heat which is obtained from the hot furnace gases is very

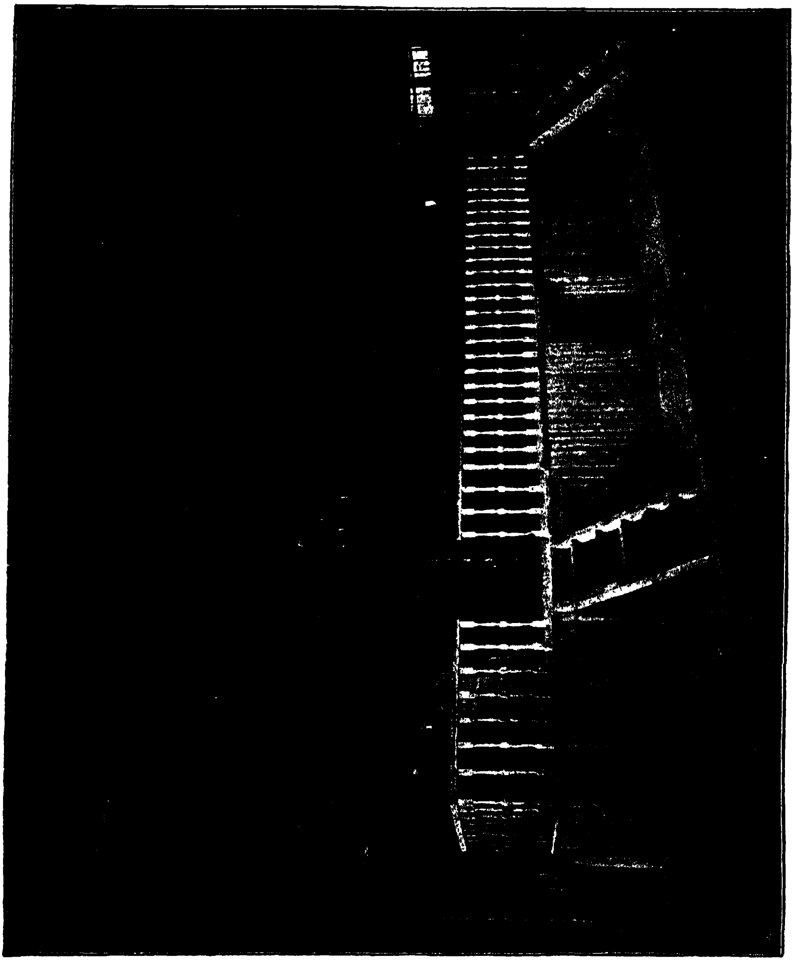


FIG. 38.—Interior of furnace house at Notodden Nitrate Works.

considerable. Witt[1] pointed out that this heat could be used in steam boilers to develop steam to drive steam turbines or electric motors and in this way to return a portion of the energy to the furnace. By perfection of the vacuum evaporators for the calcium

[1] *Loc. cit.*, p. 705.

nitrate solutions, and by more favourable heat economy in the whole process, it has now been rendered possible to return a considerable quantity of electric energy to the furnaces. The power efficiency, which only attains 3 per cent. on the average, has thus been

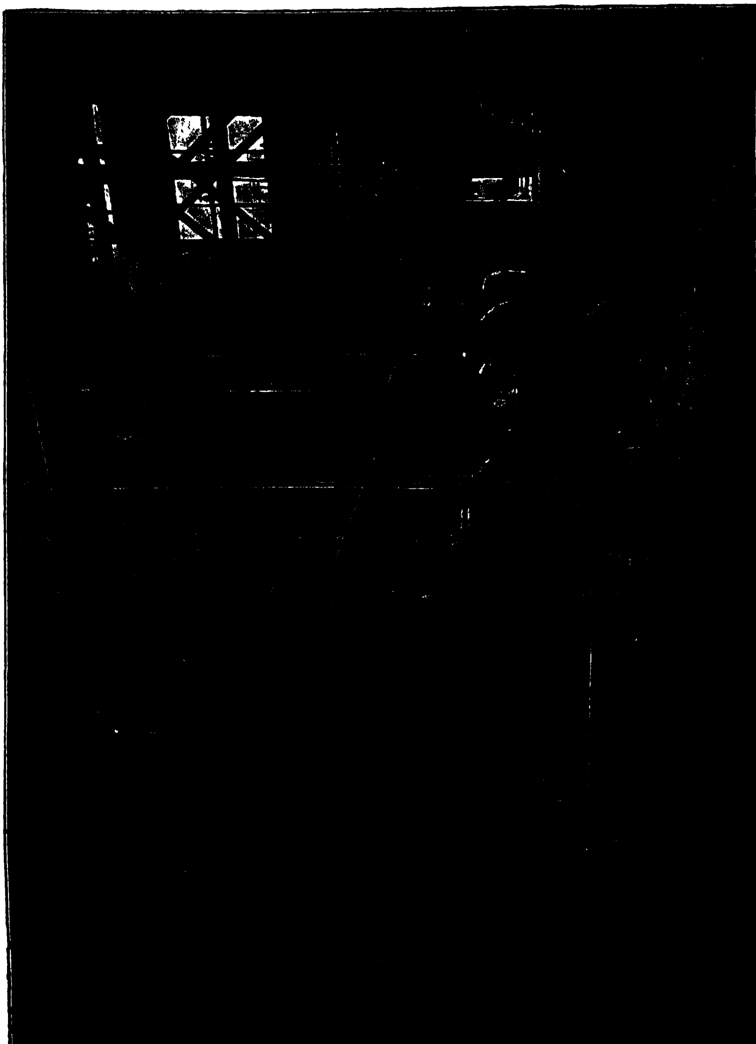


FIG. 39.—Absorption plant, Notodden.

appreciably improved. Ch. L. Parsons [1] calculates that when the arc process is used for the manufacture of 96 per cent. nitric acid, 10·8 h.p. are required per ton of fixed nitrogen.

It will be of interest if we here compare the final words of Witt's

[1] Hesse-Grossmann, "Englands Handelskrieg," iii. (1919), p. 98.

lecture on November 25th, 1905,[1] with the astonishing development which the nitrogen industry has since undergone, largely due to the impulse of the War :—

"The utilisation of synthetic nitrates will then increase quite

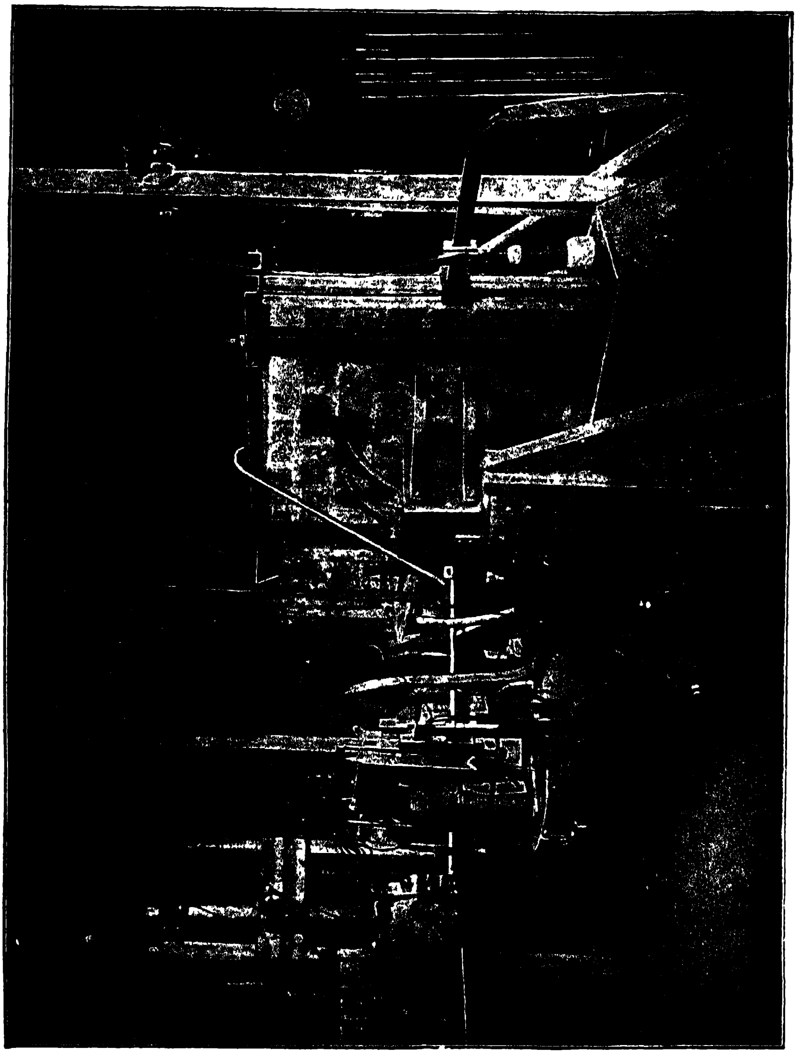


FIG. 40.—Two arc furnaces with which the earliest experiments were carried out

slowly in accordance with the rate at which the productivity of the South American nitrate deposits declines. The time which will probably be taken by this process will, it may be hoped, suffice to allow the new synthetic nitrate industry, which has become econo-

[1] O. N. Witt, *loc. cit.*, p. 706.

mically sound within the short time of three years, to grow to an extent which will enable it to meet the largest requirements with which it will be faced. For if this industry is to satisfy expectations

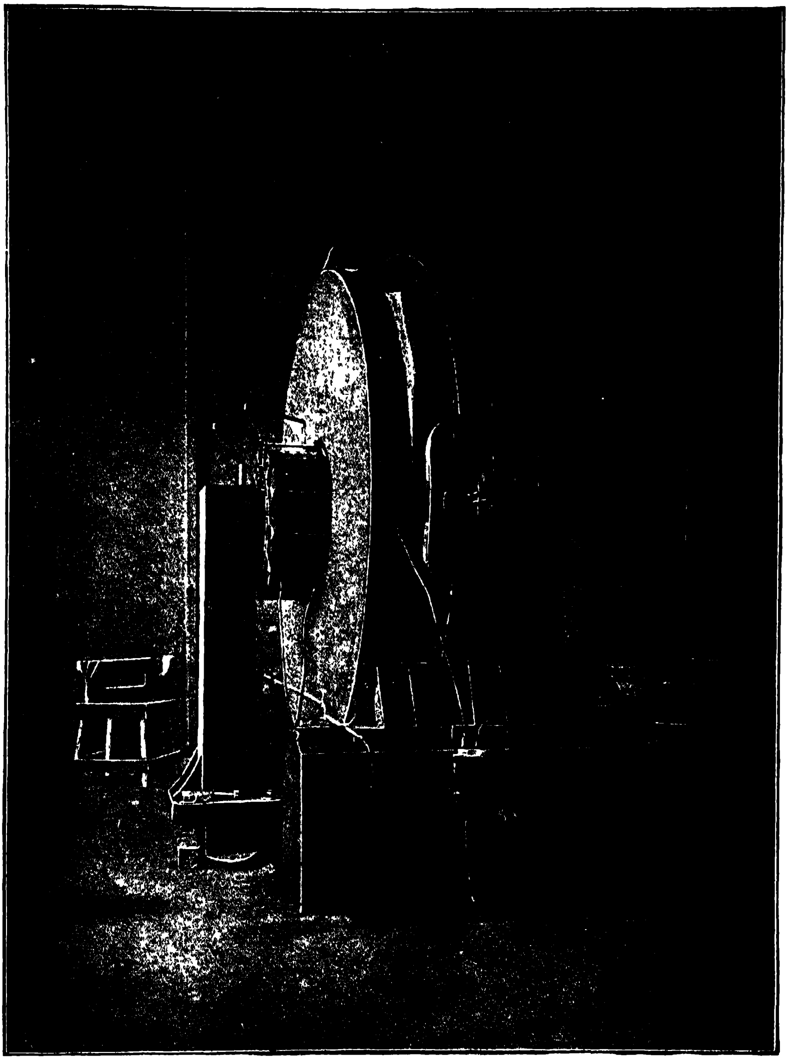


FIG. 41.—Large arc furnace during erection at Notodden.

it must ultimately be in a position to cover our total requirements of nitric acid and nitrates. . . . If it succeeds in doing this, it will be an example of the fact that the reserves which Nature has stored up for us, and which are in no case inexhaustible, were only given to us so that we might increase our knowledge and ability to such an extent

that these reserves are no longer necessary; but we are in a position to fulfil our tasks with the renewed solar energy with which

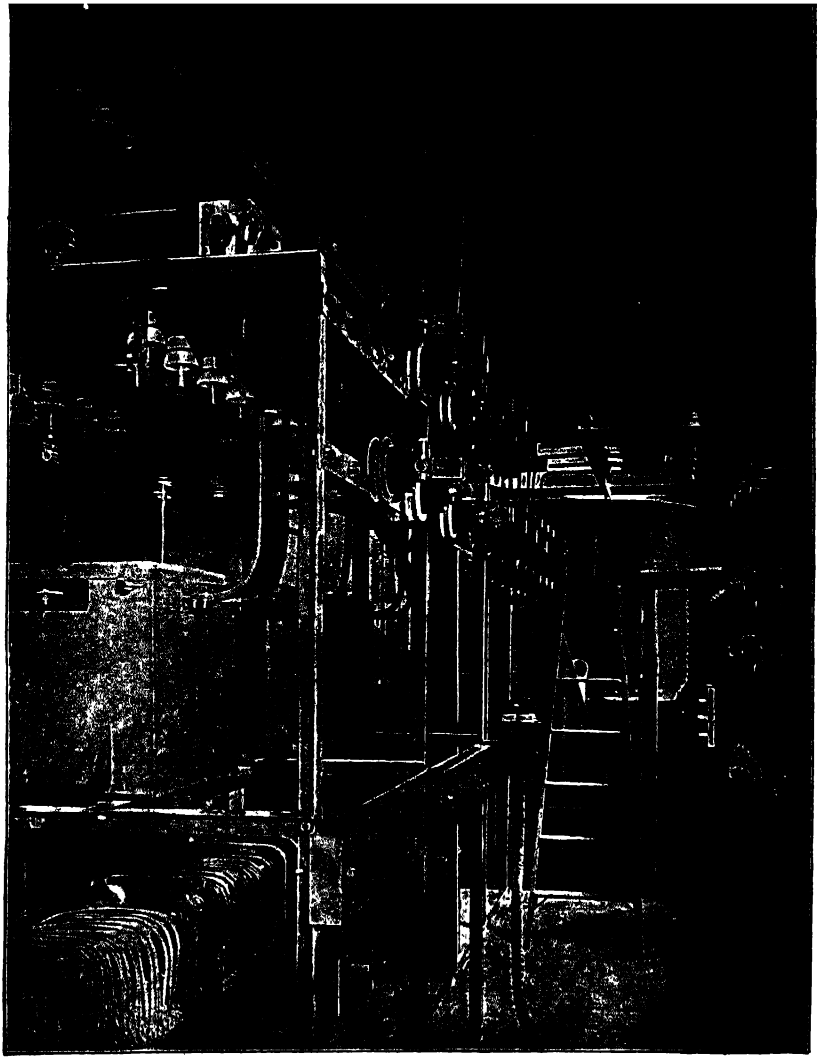


FIG. 12.—Rear of the switchboard at Notodden Nitrate Works. In background tubular boiler for utilising heat of reaction gases.

we are presented daily, in order that we may continually rise to further perfection."

Information from the Norsk Hydro[1] on the Rjukan plant is available for the year 1912. The Rjukan, Norway's largest waterfall,

[1] Pamphlets of this firm and of the Norgesalpeter-Verkaufs G.m.b.H., of Berlin.

is formed by the Maan-elf, which flows from the Mjösvand Lake and has a natural fall of 260 m. in four enormous stages and a regulated

FIG. 43 Power station, Rjukan Works.

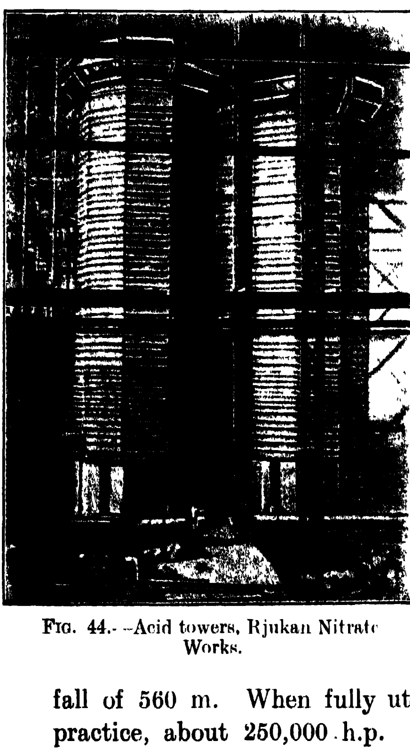


FIG. 44.—Acid towers, Rjukan Nitrate Works.

FIG. 45.—Evaporating plant, Rjukan Nitrate Works.

fall of 560 m. When fully utilised, the Rjukan Fall supplies, in practice, about 250,000 h.p. The developments required for the

utilisation of this enormous water-power were comparatively simple. The Mjösvand dam contains about 8,000 cu. m. of ferro-concrete,

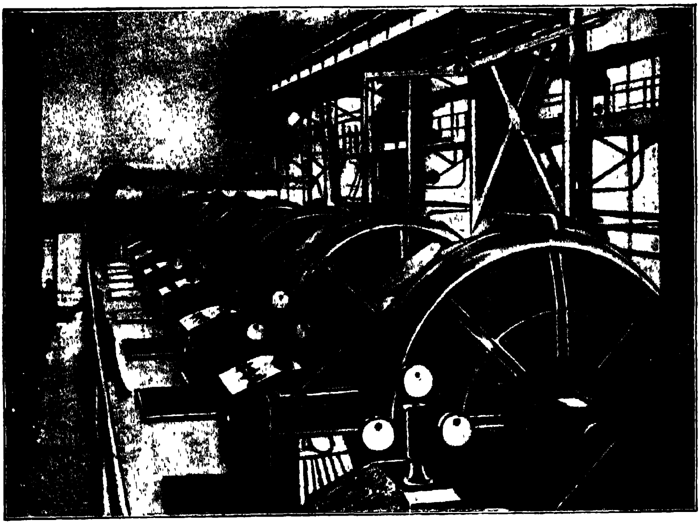


FIG. 46. -Part of furnace house, Rjukan Nitrate Works.

and retains about 800,000,000 cu. m. of water. A canal 4 km. long and of 26 sq. m. cross-section leads from this to the upper collecting basin, which feeds 10 steel tubes, each of 2 m. diameter. These carry 50 cu. m. of water per second, with which they supply the power station utilising a portion of the enormous head of the falls; the engine room of the power station covers 110 by 20 m., and contains 10 enormous double turbines, each rated at 14,450 h.p. The turbines are directly coupled with high - tension generators. These supply the works through a 10,500-volt transmission line 5 km. long. There are 60 overhead cables, which are partly of aluminium and partly of copper. The furnace-house covers 6,000 sq. m. and contains 120 furnaces, each utilising 5,000 h.p. A system of large fans is used for transporting the gases. Adjoining the furnace house is a large boiler house which covers 1,000 sq. m., and in which the heat of the hot gases from the furnaces, at a temperature of

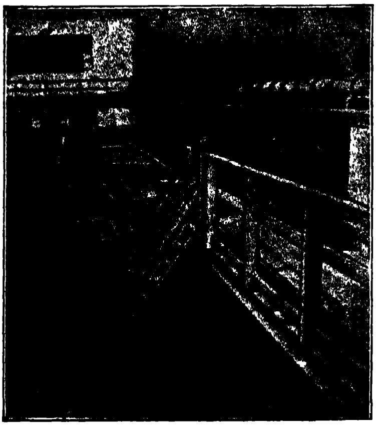


FIG. 47.—Neutralising plant, Rjukan Works.

800° C., is used for raising steam. The gases leave the boiler-house at 250° C., traverse the cooling system and several oxidation chambers, and then enter the tower house, which covers 7,000 sq. m., and is 34 m. in height. This holds 32 granite towers 7·2 m. high. The towers are filled with quartz, of which each holds 2,400 tons. The series of granite towers is followed by 14 iron towers. The towers are all fed with water, with more or less concentrated nitric acid, or with milk of lime.

The nitric acid which is obtained is converted into calcium nitrate by means of limestone contained in granite reservoirs, and the solution is concentrated in vacuum pans. The concentrated liquor which is drawn from these solidifies to form a basic salt containing about 13 per cent. N and which is comparatively non-hygroscopic. This is the finished product, which is crushed by suitable machinery and packed in wooden barrels. The Rjukan Works have their own barrel works, which cover 2,500 sq. m.

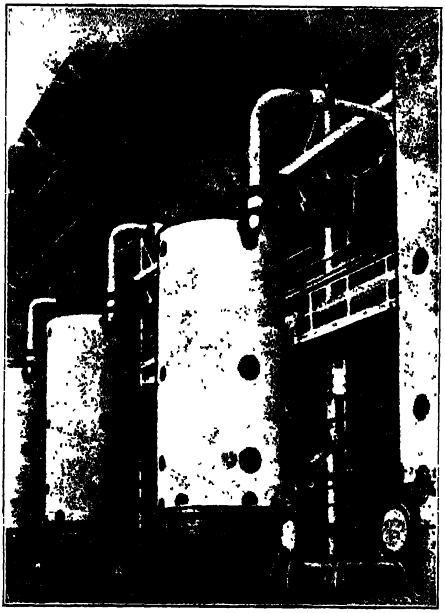


FIG. 48. Boiler house, Rjukan Nitrate Works.

The Saaheim-Rjukan Nitrate Works, of which we give illustrations in Figs. 43 to 48, is connected with Skien, the main shipping harbour, by a railway about 80 km. long and the Tin Lake which is 40 km. long. The output capacity of the Notodden and Rjukan Works of the Norsk Hydro in 1912 was about 100,000 tons of Norway nitrate annually. In that year the following water powers were actually developed and under construction :—

Working :—			
Notodden	..	65,000 h.p.	which can be developed to 95,000 h.p.
Rjukan I.	..	145,000 ,,	
Under construction			
Rjukan II.		105,000 ,,	(sufficient to produce 75,000 tons of Norway nitrate).

Under construction or projected :—

Tyin	.. ..	80,000 h.p.
Matre	.. ..	80,000 ,,

In the interval the power development of Rjukan II. has been completed.

Norway nitrate contains, on the average, 13 per cent. of N, corresponding to 76 per cent. of calcium nitrate and 26 per cent. of lime. It is, of course, free from perchlorate and other injurious constituents of Chile nitrate. It is now always despatched in sound wooden barrels containing 100 kg. net, the gross weight being 108 to 109 kg. Norway nitrate is more hygroscopic than Chile nitrate. Like the latter, it is an effective top dressing for mild winters and for all summer crops, and ensures crops which are not only luxuriant but sound and strong, in consequence of its lime contents. Norway nitrate is further used more especially for soils which are inclined to crumble, and for crops which are not hoed, more especially for sugar beet.

For winter crops it is mainly applied as a top dressing, but it is also suitable for use in this manner in the case of summer crops which are to be hoed. When employed in the spring a portion may be ploughed in. The ordinary amounts used are ½ to 1 cwt. per rod in the case of wheat and potatoes, and more in the case of turnips, according to the quality of the soil. Norway nitrate can be spread by machines such as Kuxmann's Westphalia Spreader or Vos's Spreader, or it may be spread by hand, in which case slight precautions only need be taken, such as a side wind, stout tunic, bare arms and greasing of the skin. Norway nitrate may be mixed and used with Chile nitrate, basic slag, potash salts, peat powder, ashes and so forth. The results obtained have always been entirely satisfactory.

Before the War the Norsk Hydro was already operating a plant at Notodden for the manufacture of ammonium nitrate which has been described in detail by its constructor, F. A. Bühler.[1] We will somewhat briefly refer to this plant again later. It was constructed on the lines of the ammonium nitrate works of the Sprengstoff A.G. Carbonit, of Hamburg. It was originally built for an output of 15 tons of ammonium nitrate daily. At times during the War the manufacture of ammonium nitrate was increased to an extraordinary extent.

Apart from the above-mentioned patents, the Norsk Hydroelektrisk Kvaelstof A.B., alone, and jointly with Birkeland and

[1] *Chem. Ind.*, No. 8, April 15th, 1911.

Eyde, the latter of whom is their general manager, have devised and patented a number of further processes (British Patent 3525/1905; German Patents 170,585, 179,825, 179,882, 214,445, 321,772; Norwegian Patents 14,885, 15,021, 23,542; and U.S. Patent 906,682). During the latter portion of this period special attention was paid to the absorption of the nitrous gases, and the process was adopted to some extent of direct washing with caustic soda solution or milk of lime. According to German Patent 325,636, solid nitric oxide is frozen out of the gases by intensive cooling.

Under certain conditions equilibrium is attained between nitric oxide and nitrogen dioxide [1] according to the equation

$$NO + NO_2 \rightleftarrows N_2O_3.$$

Above + 620° C. nitrogen dioxide no longer exists, but is completely dissociated into NO + O; the nearer the temperature approaches to the lower limit of + 150°, the greater does the percentage of the dioxide become, and below + 150° C. this is alone present if sufficient time is allowed for the oxidising reaction $NO + O = NO_2$. The Norsk Hydro process of manufacturing nitrite depends on the abovementioned behaviour of nitrogen oxides. If the hot furnace gases are washed with a solution of sodium carbonate or sodium hydroxide before their complete oxidation at 200° to 300° C., nitrite is obtained free from nitrate. When the gases are washed with solutions of sodium carbonate a solution of nitrite containing a large quantity of bicarbonate is finally obtained from which pure nitrite can be isolated by heating and then crystallising (German Patent 207,250). By absorbing the nitrous gases with calcium cyanamide, according to German Patent 206,949, calcium and ammonium nitrates are obtained.

According to Norwegian Patent 22,894 aluminium is used instead of stoneware as a constructional material in the manufacture or transport of nitric acid so long as the concentration of the acid is below 65 per cent., and it contains less than 5 per cent. of nitrogen oxides. German Patent 264,393 deals with the utilisation of the waste heat from the furnace; Norwegian Patents 23,058 and 23,575 with the increased concentration of nitric oxide obtained by catalytic action, and Norwegian Patent 23,545 with the conversion of crude calcium nitrate into a powder.

According to French Patent 459,746 the most advantageous mixture of nitrogen and oxygen is introduced into the active reaction zone of the furnace, whilst outside this zone cheaper mixtures or air itself are introduced in the form of a vortex surrounding the arc.

[1] Vgl. K. A. Hofmann, "Lehrbuch der anorgan. Chemie" (Brunswick, 1919), 2 Aufl., pp. 116 *et seq.*

By distillation dilute nitric acid of about 30 per cent. strength can be concentrated step by step to obtain acid of 40, 50, 60 or 68 per cent., the distillate being condensed in a dephlegmator from which it returns to the evaporators through a special contrivance (French Patent 463,859; German Patent 278,867).

According to British Patent 15,934/1912 and German Patent 268,828, concentrated calcium nitrate solutions are easily converted into solid form by cooling them under certain definite conditions and adding powdered calcium nitrate. The product obtained by this process consists of thin sheets which do not adhere to one another (see also French Patents 465,504 and 465,739). French Patent 408,506 deals with the manufacture of ammonium nitrate by the interaction of ammonium sulphate and calcium nitrate. Norwegian Patent 31,408 deals with the manufacture of fertilisers consisting of calcium-urea nitrates.

The name "Norge salpeter" is criticised by Dafert,[1] who recommends the term *Kalk salpeter* (calcium nitrate) as being the only one which is suitable. The following average analysis is given in a report on the activities of the Agricultural Research Station at Speyer for 1910 [2]:—12·5 per cent. N, 25·6 per cent. CaO, 22·3 per cent. water, 1·7 per cent. insoluble constituents. In a communication from the laboratory of the Rjukan Nitrate Works, N. Busvold [3] gives the following analysis:—

	Per cent.		Per cent.
$Ca(NO_3)_2$	76·15	$MgCO_3$	0·35
$Ca(NO_2)_2$	0·05	Fe_2O_3	0·10
CaO	0·15	Al_2O_3	0·40
MgO	0·30	Insoluble	0·50
$CaCO_3$	0·55	Water	21·45

S. Hals [4] has published very interesting investigations on the hygroscopic character of calcium nitrate. As ordinarily packed in wooden drums lined with thick paper, Norwegian nitrate absorbed 3 per cent. of moisture in one year and no loss of nitrogen occurred. At both ends of the barrel the salt had caked to a depth of 5 to 10 cm., but without becoming hard or losing its value as a fertiliser.

O. Herrmann [5] states that at Notodden the Norsk Hydro also decomposes phosphates with nitric acid by Bretteville's process (German Patent 217,309). According to Birkeland's Norwegian Patent 24,423, dilute nitric acid may advantageously be used for the

[1] *Chem. Ztg.*, 1913, p. 716.
[2] *Ibid.*, 1911, p. 1180.
[3] *Ibid.*, 1914, p. 799.
[4] *Ibid.*, 1911, p. 1130.
[5] *Ibid.*, 1913, p. 919; see also p. 303.

extraction of ores (see also French Patent 451,291). The solutions which are obtained are precipitated with lime, by which means the metallic hydroxide is obtained together with calcium nitrate as a by-product. According to German Patent 276,814 and French Patent 456,786, crude phosphorite is decomposed by nitric acid and neutralised with lime. The unfiltered solution is evaporated *in vacuo* at a temperature not exceeding 70° C. The product contains 7 to 8 per cent. of nitrogen and 20 per cent. of phosphoric anhydride. As is well known, the Norsk Hydro, jointly with the Norsk A.B. for Elektrokemisk Industri, formed the "Labrador" Company with a share capital of 2,000,000 kr.[1] for the purpose of decomposing Norwegian labradorite with nitric acid in order to manufacture alumina and calcium nitrate.

In this connection we may also refer to a process described in U.S. Patent 1,057,876 of S. Peacock and the Southern Electrochemical Company, New York, according to which ground phosphate is mixed with water to a thin paste and then directly exposed to the nitrous gases from an electric furnace until these no longer show an acid reaction. Calcium nitrate is obtained together with insoluble di-calcium phosphate, which may be used as a fertiliser:—

$$4HNO_3 + CaO.Ca_3(PO_4)_2 = 2Ca(NO_3)_2 + 2CaHPO_4 + H_2O.$$

According to German Patent 284,741, H. Büeler de Florin leaches copper ores containing lime and magnesia with the aid of nitrous gases or dilute nitric acid. Norwegian Patent 25,057 and British Patent 5,184/1914 describe processes which are somewhat similar In German Patent 324,263 the Norsk Hydro has latterly described a process of concentrating sulphides in ores by means of a preliminary fusion with silicon and pyrites. H. Büeler de Florin [2] has discussed at length the chemical questions associated with the use of nitric acid According to him, the leaching of ores with nitric acid is only justified when the composition of the ores and the local circumstances exclude the possibility of hydraulic treatment, direct fusion, and the erection of a sulphuric acid works or the provision of sulphuric acid. The following equations indicate the principle of the more important processes in question:—

Process of:	Treatment.
Kingsley . .	$3PbS + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O + 3S$
Rankin . .	$3PbS + 8HNO_3 = 3PbSO_4 + 8NO + 4H_2O$
Norsk Hydro .	$Bi_2O_3 + 6HNO_3 = 2Bi(NO_3)_3 + 2H_2O$
Büeler . .	$CuCO_3 + 2HNO_3 = Cu(NO_3)_2 + H_2O + CO_2$

[1] *Chem. Ztg.*, 1919, p. 311.
[2] *Ibid.*, 1914, p. 926.

Process of:	Regeneration of the Acid.
Kingsley	$Pb(NO_3)_2+Na_2CO_3=PbCO_3+2NaNO_3$ $2NaNO_3+H_2SO_4=Na_2SO_4+2HNO_3$
Rankin	$2NO+3O+H_2O=2HNO_3$
Norsk Hydro	$Bi(NO_3)_3+H_2O=BiO.NO_3+2HNO_3$
Büeler	$Cu(NO_3)_2=CuO+N_2O_5$ (summarised) $N_2O_5+H_2O=2HNO_3$

There are numerous other patents by the Norsk Hydro which deal with the development of their electric process. In German Patent 295,766 a high-pressure arc furnace is described which is connected with a pressure equalising container which also serves for cooling the gases. This may also be submitted to external pressure, and may take the form of the fire tube of a steam boiler. The heat energy from the arc furnace may be utilised in a hot-air turbine and condenser (German Patent 298,898). Radial coupling of the furnaces is recommended in order to increase the stability of the arc (German Patent 298,697). In German Patent 310,859 a circulatory system is described which supplies to the arc air as rich as possible in oxygen. Finally in German Patent 321,772 a process is described of introducing air into the furnace in such a manner that the life of the electrodes is increased.

According to German Patent 300,897 the nitrous gases are absorbed by concentrated sulphuric acid, and the nitrosulphuric acid which is obtained is decomposed by nitric acid vapours, forming concentrated nitric acid, on the one hand, and concentrated nitrous gases, on the other. The absorption of the nitrous gases from the furnace can, of course, also be effected by suitably prepared limestone (German Patent 284,042; French Patent 465,740). If the gases are absorbed by alkali carbonate or bicarbonate, the nitrate solutions which are obtained may be caused to react with ammonium chloride to form ammonium nitrate and alkali chloride, according to German Patent 302,034; if sodium chloride is used, it may then be reconverted into bicarbonate and NH_4Cl by the ammonia soda process. Calcium nitrate may be converted into a non-dusty form, according to German Patent 287,307.

The experiments carried out in the laboratories of the B.A.S.F. at Ludwigshafen under the direction of H. v. Brunck, which were started in 1897, on the arc synthesis of nitric acid, led in 1905 to the discovery of a suitable process by O. Schönherr; Hessberger co-operated with Schönherr on the electro-technical aspect of the process.

The success of the magnetic furnace of Birkeland and Eyde had led to the opinion that it was advantageous to use an intermittent arc which fluctuated very rapidly and so caused turbulence in the

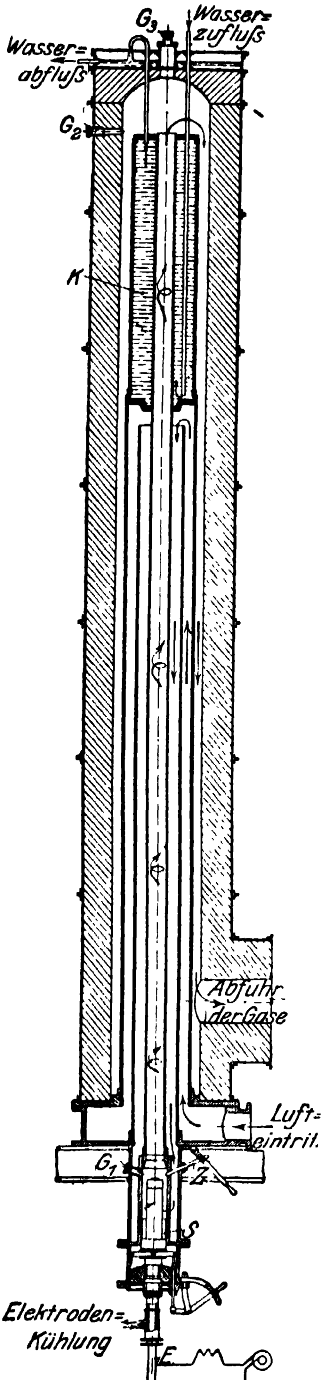
surrounding air. The Schönherr process of the B.A.S.F. involves the use of a perfectly steady and stable arc using a very large quantity of current.

Schönherr [1] and Bernthsen [2] have described the experiments of the B.A.S.F. We must refer here to these original accounts, which include very complete drawings.

In the first place, Schönherr and Hessberger showed that an alternate current arc, which is the only practical form, is very unstable. It is not possible to blow a large amount of air through it as otherwise it would be blown out; consequently very dilute reaction gases are obtained. High concentrations of the product may, however, be obtained by carrying the air along the arc and in close proximity to it. Even in this case, however, a very small disturbance or a lateral air current may suffice to extinguish the extremely unstable arc. "The pulsation of the current itself, its fluctuations from zero to the maximum, its reversal and flow in the contrary direction, cause such very large disturbances in an otherwise regulated air supply that it might be supposed to be impossible to solve this problem in a satisfactory manner. A direct current arc can be much more easily maintained. However, by the use of a special expedient all difficulties due to the alternating current arc can be overcome. If the air is circulated in the form of a spiral instead of in a straight line, that is, if it is caused to traverse the surface of the arc in the direction of a screw, even the alternate current arc loses its instability. It then burns as steadily as a candle-flame, and can be enclosed in a fairly narrow metal tube without touching the walls. An arc along which the air passes in a straight line has on the other hand a tendency to strike on to the walls. A metallic tube can therefore not be used to enclose such an arc."

The apparatus used by Schönherr and Bernthsen to demonstrate the process is very simple. Inside the tube there is an electrode insulated from the same. Air is passed through the tube with an eddying motion and the arc is lighted by decreasing the distance between the insulated electrode and the wall of the tube, so that a spark passes at a certain point. The air current then drives this short auxiliary arc upwards and a steady arc is obtained which passes along the whole length of the tube and is surrounded by an eddying air current. Its upper end is at a considerable distance from the insulated electrode—namely, at that point where the gases have attained such a temperature that they conduct the current, which therefore passes through them. As soon as the arc is once started,

[1] *Elektrotechn. Zeitsch.*, 1909, Nos. 16–17.
[2] *Zeitsch. f. angew. Chem.*, 1909, p. 1167.



at a voltage of about 5,000, it has very seldom to be restarted, as it is very stable. No further current passes at the ignition point, as the voltage drops considerably during burning. The small arc of the demonstration apparatus used about 7 k.w. (10 h.p.).

The industrial plant is similar to the laboratory apparatus (Fig. 49). The insulated electrode consists of a strong water-cooled copper sleeve, through which an adjustable iron rod *E* is inserted, which forms the actual electrode. The arc starts from this point, and the iron rod is gradually worn away. At the temperature of the arc the iron is gradually converted into magnetic oxide, which covers the rod with a molten surface layer which slowly evaporates. The rod is adjusted to compensate for the wastage of the iron. This wastage is extremely small and is of no practical importance. The cost of the electrode rods amounts to a few pfennig only per kilowatt year. The electrodes lasted, for example, for 2,000 working hours—that is, for over three months. The insertion of a new electrode is very simple, as it is simply screwed to the old one, and the replacement only requires 15 minutes. The water-cooled copper sleeve is so far removed from the wall of the tube that no passage of current need be feared. The arc is started by means of the starting lever, *Z*. By its means

FIG. 49.

Wasserabfluss = Water outlet.
Wasserzufluss = Water Supply.
Abfuhr der Gase = Outlet for gases.
Lufteintritt = Air supply.
Elektroden - Kühlung = Electrode cooling jacket.

a massive iron rod, Z, is caused to approach the electrode, E, from the wall of the tube to such a distance that a spark passes. As the whole casing of the furnace, with the exception of the central electrode, E, is earthed, striking the arc is accompanied by no danger to the operator.

The point of ignition can be observed through the sight hole, G_1, and it is thus possible to adjust the electrode, E, as required. The air, which is pre-heated by having to traverse a definite path through the inside of the furnace, passes into the actual combustion chamber through several rows of tangentially bored holes in the tube. The air current can be regulated by the damper, S, and in this way the length of the arc and consequently the load on the furnace can be varied at will.

In a 600-h.p. furnace the arc has a length of about 5 m., and a length of about 7 m. in a 1,000-h.p. furnace. The surrounding tube is of ordinary iron, and lasts indefinitely. The upper portion of the tube is provided with a water-cooling system, K. By adjustment of the damper, S, the arc is driven up the tube till it ends in this portion. The sight holes, G_2, and G_3, serve for observation of the action of the furnace. Through G_3 it is possible to see along the axis of the arc, and it is then seen how the upper end of the arc continuously rotates in a circle. The arc fluctuates slightly in length and strikes a comparatively large area of the water-jacket and the wear and tear of the latter is therefore very small. It is also so constructed that it can easily be repaired, and it is only necessary to screw in a new tube. After four months' working scarcely any wear could be observed on the water jackets.

After passing the coolers the hot reaction gases pass along a brickwork channel, armoured externally with iron rings, which surrounds the internal tube concentrically, and then enter the exit main. As in the installations previously described, this leads to a boiler which serves as a cooler and at the same time supplies the necessary steam for concentrating the liquors.

The untreated air is pre-heated by the reaction gases, which it cools during its upward course, and is further heated on reversing its direction when passing downwards immediately outside the inner tube; finally it enters into the inner tube through the tangential perforations already referred to, after being thoroughly preheated.

The furnaces can also be operated in a horizontal position without any disadvantage. It is also quite unimportant whether the air passes through the reaction zone upwards or downwards. If the tube is made short enough, and the far end is left open, a large hot blast is obtained of strongly oxidising properties which may be used for

smelting processes. The arc need not necessarily be rectilinear, but may be curved.

On the large scale it is only necessary to restart the arc under exceptional circumstances, such as fluctuations in the air supply, loss of voltage, short circuits and so forth. The current and voltage curves are almost pure sine curves. Fig. 50*a* is a voltage curve of the Schönherr arc, while Fig. 50*b* shows that of an ordinary arc lamp, and Fig. 50*c* that of a Birkeland-Eyde arc. The reversal peak, which is clearly shown in *b* and *c*, is absent in *a*, the two limbs of which show very little irregularity. The power factor, cos ϕ, of the Schönherr arc is 0·92 to 0·96, *i.e.*, very nearly unity. Practically the same air particles transmit the current during several alternating periods, and therefore the fluctuations in the resistance are as small as in an ordinary arc. In the Schönherr furnace the air is in contact with the arc during a much longer period than in the Birkeland-Eyde furnace. For these reasons the power efficiency in the Schönherr furnace is much more favourable than in the Birkeland-Eyde furnace, but in spite of this only 3 per cent. of the total power is used for the production of nitric oxide.

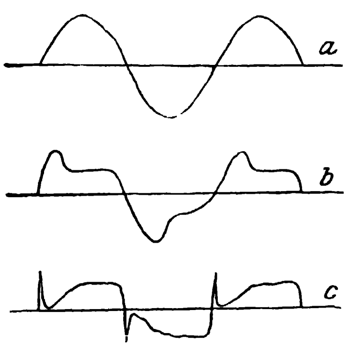


FIG. 50.—Oscillographs of arc voltages. (Schonherr.)

It is not possible to pre-heat the air in iron tubes to a temperature much higher than 500° C. The best yields of NO are obtained by admitting hot air just above the electrode and cold air at a somewhat higher point. The latter is heavier and therefore clings to the tube wall on account of the eddy current.

The heat balance of the Schönherr furnace shows that about 40 per cent. of the heat is recovered in the form of hot water, 17 per cent. is lost by radiation, 30 per cent. is utilised in the steam boiler, a further 10 per cent. has to be removed from the gases by water cooling behind the boiler, and 3 per cent. alone produces nitric oxide. The construction of the furnaces is simple and cheap. They contain no moving parts, and are suitable for the erection of large working units. The yields are good, and the concentrations of nitric oxide are higher than those obtained by most other processes. At temperatures below 1,200° to 1,500° C. nitric oxide is fairly stable, so that it is sufficient to cool below this limit in order to stabilise the equilibrium. In the Schönherr-Hessberger furnace, the gases leave the actual reaction zone at a temperature about 1,200° C. On entering

the outlet main they still have a temperature of about 850° C. At temperatures below 600° to 620° C. the oxidation of the colourless nitric oxide to the brown dioxide commences, but is only completed below 140° to 150° C.; the completion of this reaction takes some considerable time. The lower the nitric oxide concentration in the gaseous mixture the longer does the reaction take. A mixture containing 2 per cent. of NO at 20° C. requires 12 seconds for the oxidation of 50 per cent. of the amount, but 100 seconds until 90 per cent. is oxidised.

The methods employed for absorbing the nitric oxide are not essentially different from those used by the Norsk Hydro. The gases coming from the boiler house pass through coolers into large oxidising chambers in which the nitrogen dioxide is formed. They then pass into granite towers 20 m. high, which are filled with lumps of quartz. Water or dilute nitric acid is pumped up and trickled down these towers, and as a final product nitric acid of about 40 per cent. strength is obtained. This may be converted into concentrated acid by the addition of salts which combine with water or of concentrated sulphuric acid. The acid towers are followed by alkaline absorption towers, down which milk of lime or soda solution is trickled, and in which mixtures of nitrate and nitrite are produced. German Patent 188,188 of the B.A.S.F. claims the production of pure nitrite by suitable methods of absorption. By cooling the reaction gases below 0° C., liquid NO_2 may be obtained. A portion of the nitric acid from the towers is converted into calcium nitrate solution by means of limestone; this solution is concentrated in vacuum pans until it solidifies on cooling. The solidified cakes are ground in mills and form ordinary Norway saltpetre containing 13 per cent. of nitrogen.

In an interesting paper [1] read before the Berlin Electro-Technical Association on January 13th, 1909, Schönherr points out that the difficult absorption of dilute nitrous gases may be facilitated by the addition of ozone. The slow absorption of the nitric oxide which takes place under ordinary conditions is due to the slowness of the oxidation of nitric oxide to the dioxide, which occurs instantaneously with ozone, and it is even possible to carry the oxidation to the stage of nitrogen pentoxide; the practical application of the process is dependent on a sufficiently cheap method of producing ozone. Schönherr also emphasises the fact that the arc synthesis of nitric acid might open up a direct method of extending cultivation, as nothing further is required than cheap electric power, and limestone districts might be opened up by its means which have so far been

[1] *Elektrotechn. Zeitsch.*, 1909, Nos. 16–17.

economically inactive in consequence of their geographical position and lack of coal.

Bernthsen [1] expressed himself as follows on the atmospheric nitric acid industry at the Seventh International Congress of Applied Chemistry in London in 1919, pointing out that the smoky chimneys of ordinary industrial activities are not required for the purpose: "The circumstance should not be ignored that the new industry of atmospheric nitric acid will play no part in the large-scale exploitation of natural resources which is characteristic of industries based on the use of coal formed during past ages. The new industry depends for its energy on water, 'white coal,' the utilisation of which involves no depletion of stored resources, as this source of power is continuously renewed, according to the words of the poet

"'Von Himmel kommt es, zum Himmel steigt es,
Und wieder nieder zur Erde muss es,
Ewig wechselnd!'" [2]

The power resources available at Ludwigshafen for the experimental development of the Schönherr-Hessberger furnace were so restricted that a furnace of not more than 300 kw. had to be used. Consequently as soon as the process had proved satisfactory in its main details, operations were commenced at an experimental works at Fiskaa near Kristianssand in South Norway in 1907. The B.A.S.F., as representatives of the German dyestuff manufacturers, concluded an agreement with the Norsk Hydro in 1906 for the joint operation and development of the Rjukan Works. The Schönherr-Hessberger furnaces (Fig. 51) of the Kristianssand plant were found to be entirely satisfactory. Power was obtained in the form of three-phase current from a power station at Saeterstal, 56 km. distant, and at a voltage of 25,000 volts. In the works the voltage was transformed to 7,200 volts, the phase voltage being 4,200 volts. The furnaces were radially coupled. About 1,300 kw. were available at the works. During normal working three furnaces were operated, each consuming 600 h.p. The arcs used were 5 m. long. A furnace was also temporarily tried consuming 1,000 h.p. with an arc 7 m. long. A furnace consuming 2,000 h.p. is said to be equally practicable. At Kristianssand absorption is carried out by the process already described.

As the power supply at Kristianssand was also insufficient, the 1,000 kw. furnaces intended for Rjukan, treating 1,100 cu. m. of air hourly, were tested at Notodden whilst connected up as was proposed for Rjukan. The results obtained at Notodden were satis-

[1] *Zeitsch. f. angew. Chem.*, 1909, p. 1167.

[2] "From heaven it falls, to heaven it rises,
And ever again to earth it falls,
Constantly changing."

factory, and the furnaces were transferred to the Rjukan plant, the first portion of which started in 1911.

By this date, however, the B.A.S.F. had established the fact that Haber's ammonia synthesis would prove a satisfactory method of nitrogen fixation. As the simultaneous development of both processes would have involved enormous sums of money, the German firms withdrew from their agreement with the Norsk Hydro. The liquidation of their Norwegian interests was almost concluded by 1912. The purpose of the association had been development of the new industry, the exploitation of favourable water-powers, and the avoidance of competition between the parties in the development of their several patent rights outside Norway. The disposal of licences for both processes was finally left entirely in the hands of the B.A.S.F. With the cancellation of the agreement, these arrangements naturally lapsed. The arc-process patents of the B.A.S.F. were sold to the Norsk Hydro, which mainly worked with French capital. In the spring of 1912 about 100,000 h.p. were being utilised in furnaces each consuming about 1,000 kw. at Rjukan and constructed on the Schönherr-B.A.S.F. system. The scheme of the B.A.S.F. to develop about 50,000 electric h.p. for the arc synthesis by diversion of the River Alz into the Salzach, for which a concession had already been applied, was never carried out, on account of the great development of the Haber-Bosch process.

FIG. 51.—Schonherr furnace room at Kristianssand.

The Schönherr-Hessberger furnace is protected by a large number of patents [1] (German Patents 201,279, 204,997, 212,051, 212,501, 227,013, 229,292, 238,367, 238,368, 255,732, 265,413 ; Austrian Patents 27,789, 27,790 ; French Patents 348,791, 357,538 ; British Patent 26,602/1904). The B.A.S.F. hold an equally large number of patents on the absorption of the nitrous gases,[2] of which a few only can be dealt with here. According to German Patent 188,188

[1] Herrmann, *Chem. Ztg.*, 1913, p. 918.
[2] *Loc cit*, p. 920.

pure nitrite only is readily obtained from these gases at 300° C., and can, if desired, be converted into nitrate with evolution of nitrogen oxides by treatment with nitric acid (German Patent 220,539). In German Patent 238,369 and French Patent 411,674 a process is described of producing pure nitrate from mixtures of nitrate and nitrite. Calcium nitrate may be obtained in a form which is more easily spread by converting it into the urea double salt (1 : 4) (German Patent 295,548).

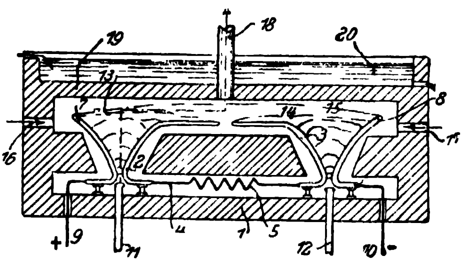


FIG. 52.—Pauling arc furnace (German Patent 216,090).

The most interesting process, apart from those of Birkeland and Eyde and the Schönherr-B.A.S.F. process, is that of Pauling and the Salpetersäureindustrie G.m.b.H. of Gelsenkirchen, which has been discussed in detail by F. Russ.[1] Electrodes are used resembling forked lightning conductors, between which the electric arcs, which may be about 1 m. long, are driven upwards by an air current. At the narrowest point the arc is relighted, after being blown out, by means of auxiliary electrodes (German Patent 196,829). Fig. 52 depicts a furnace with two pairs of horned electrodes, as described in German Patent 216,090. The pairs of electrodes are numbered 7–2 and 3–8. These pass through the floor, 1, of the furnace, from which they are insulated, and are here connected to one another by the main, 4, through the resistance, 5. The outer electrodes 7 and 8 are connected to the busbars, whilst the inner electrodes 2 and 3 are so extended that they are almost in contact. The air enters through jets 11 and 12, and blows the arc upwards to a united long and quiet flame. 16 and 17 are the entry ports for the main portion of the air to be oxidised, which leaves the furnace at 18. The inner wall of the furnace is of masonry, and is provided with the water cooler, 20. The arc is struck by blade-shaped auxiliary electrodes carried by slits in the forked electrodes,

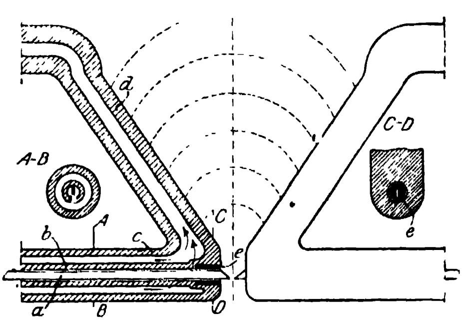


FIG. 53.—Pauling's arc-striking blades (German Patent 269,238).

[1] *Chem. Ztg.*, 1909, p. 482.

and which can be approached at high tension to within 1 to 2 mm. of one another. When the smallest distance between the main electrodes is 40 mm., the high tension arc is extended to a length of 1 m. The furnace here represented treats 600 cu. m. of air hourly.

Fig. 53 shows the arrangement of the blade-shaped striking electrodes according to German Patent 269,238. Cold water circulating between walls *b* and *c* enables the main electrode *d* and the auxiliary electrode *a* to be cooled intensively. The latter is fixed into the cooling tube by the screwed terminal *e* in such a manner that it is maintained in the necessary absolutely horizontal position (see also German Patent 258,385).

The first Pauling installation was that of the nitric acid works at Patsch, near Innsbruck, the property of the Luftverwertungs G.m.b.H., Innsbruck. These adjoin the Sill Power Station of the town of Innsbruck, and utilise about 10,000 h.p. The main products are nitric acid of various commercial strengths and high-grade sodium nitrite. The current is transformed from 10,000 to 4,000 volts. The installation comprises 24 furnaces of masonry, each of which contains two arcs ; these furnaces are arranged in groups of three. They consist of simple shafts constructed of acid-proof material into which the electrodes are built. These are constructed of copper, are water-cooled, and diverge at an angle of 60° ; at the point of nearest approach they are provided with auxiliary electrodes of sheet copper which serve to strike the arc. Air at ½ atm. pressure is blown in by a jet below the auxiliary electrodes and expands the arc flame. The furnace is so arranged that the reaction mixture is cooled as rapidly and thoroughly as possible behind the reaction zone. The furnaces have an average capacity of about 800 h.p., and yield about 60 gm. of HNO_3 of 100 per cent. per kilowatt-hour.

The regulation of the furnace is extremely simple. This is effected by turning a handwheel, which causes the auxiliary electrodes, which are slightly worn away by the arc, to approach one another. The current is switched on with an ordinary lever switch, so that no time is lost in putting a furnace in or out of action. By maintaining a sufficient number of furnaces in reserve it is possible to maintain a constant load at the power station. German Patents 193,366 and 213,710 describe a system of electrical connection which enables any number of arcs to be arranged in parallel or in series. This enables the disposition to be accurately adjusted to comply with varying circumstances.

The furnaces at Patsch work at a voltage of about 5,000 and attain a total power factor, cos ϕ, at the generators of the power station of 0·7. The figure obtained for cos ϕ at the actual furnaces is 0·98.

The high velocity air current between the electrodes carries the arc up these during each half-period of the current, and thus rapidly extends it in length. The arc breaks as soon as it has attained such a length that its voltage is greater than that corresponding to the distance between the two auxiliary electrodes. A new arc is immediately formed between the auxiliary electrodes and is similarly driven upwards and extinguished. As a current of 42 periods per second is used, this process is repeated 84 times per second. At this periodicity the alternation escapes the eye, and the whole appears as a complete disc of flame.

The temperature varies from 2,500° to 3,000° C. according to the distance between the auxiliary electrodes. It is still 1,200° to 1,300° C. in the flues of the furnace. The hot gases, containing 1·5 to 2 per cent. of NO by volume, are passed under boilers, where a portion of the heat is utilised. They then pass through heat interchangers in which the intake air is pre-heated to about 300° C. The gases are then further cooled by special coolers to a temperature at which the NO is oxidised to NO_2 in large chambers. This reaction is complete after a certain time interval.

The gases then pass into a system of scrubbing towers arranged in series and constructed of acid proof material, each of which has a diameter of 5 m. and a height of 10 m. These towers contain a filling which offers a large surface, down which water or acid from the succeeding tower trickles in such a manner that the whole surface of the packing is uniformly wetted. The gases ascend the towers from below. In the first tower an acid of 30 to 40 per cent. is obtained which is concentrated to the usual commercial strength in concentrating pans which utilise the waste heat from the furnaces. By a special process described in German Patent 257,809, the gases from the main system can be completely concentrated to a strength of 98 per cent. This acid is chemically pure and suitable for every purpose (German Patents 257,809, 274,165, and British Patent 22,320/1913).

The gases escaping from the acid absorption towers traverse several further towers which are fed with sodium hydroxide solution and in which the remaining nitrous gases are converted into sodium nitrite. Pure nitrite is obtained from the wash liquors by evaporation and crystallisation.

The furnaces are provided with sight holes covered with mica, one man being required for the supervision and operation of six units. If the copper electrodes are replaced by iron electrodes, these are very rapidly covered with a protecting layer of oxide. They have a life of about 200 working hours.

The main advantages of the Pauling process are the fixed position of the electrodes and the extremely simple regulation of the arc. In order to develop the process further, a works was erected at Legnano, near Milan, in 1908, to utilise 10,000 h.p., and another at La Roche de Rame in Southern France. R. Hoffmann [1] has described in detail the works at Patsch and the new installation of the Southern Power Company at Great Falls in North America.

The Bayrische Luftsalpeter G.m.b.H.,[2] of Munich, was founded in order to manufacture nitrate by the Pauling process in conjunction with important water powers at Feldafing.

The further development of the process is associated with the following patents of the Gelsenkirchener Salpetersäureindustrie G.m.b.H. and H. Pauling: German Patents 184,958, 186,454, 187,367, 193,402, 198,241, 202,763, 203,747, 205,464, 231,584, 235,299, 241,882, 250,968, 258,385; U.S. Patents 877,446, 877,448, 882,958, 887,220, 887,266, 898,133, 898,390; British Patents 7,869/1906, 8,452/1906, 18,599/1906, 18,900/1907, 18,901/1907.

According to German Patent 205,018 commercial nitric acid of at least 60 per cent. strength is obtained directly from the nitrous gases by cooling them to below 0° C. If they are sufficiently cooled, liquid nitrogen dioxide is obtained of boiling point 22° to 23° C. and melting point − 9° C. The installation of the Elektrosalpeterwerke A.G. at Zschornewitz, near Bitterfeld, utilised 33,000 kw. for a similar process. Toluene was used as a cooling medium for use in refrigerating machinery. The liquid nitrogen dioxide was collected in large earthenware containers, from which it was conveyed by compressed air to the actual nitric acid plant. An explosion occurred in June, 1917, which destroyed the whole of the Zschornewitz Works, leaving only the main walls standing [3]; this may have been due to leakage of the cooling plant, permitting nitrogen dioxide to come into contact with oil residues and with toluene vapour. The very violent explosion was apparently intensified by the entry of burning toluene into the nitrogen dioxide reservoirs. The same system has been employed without any difficulty by the Rhina Works of the Nitrum A.G., utilising 13,000 kw. The electric furnaces used at Zschornewitz, by the Nitrum A.G. at Rhina, and the Swiss Nitrum A.G. at Bodio, where 9,000 kw. are used, were constructed by the Elektrochemischen Werken G.m.b.H., and F. Rothe. At the condensing plant at Bodio a violent explosion occurred in the autumn of 1921, which emphasised the danger of the system.

According to German Patent 196,112, British Patent 7,871/1906

[1] *Chem. Ztg.*, 1913, pp. 1310 *et seq.*
[2] *Ibid.*, 1921, p. 207.
[3] *Ibid.*, 1919, p. 621.

and U.S. Patent 877,447, water or steam is added to the hot reaction gases in such quantity that liquid nitric acid only separates below 100° C. It is thus possible to work with plant of metallic construction above this temperature, and to confine the use of stoneware, which is less efficient, to the cooler portion only of the plant. The acid so obtained, is, however, never stronger than 53 per cent. There is an interesting patent by H. Pauling—namely U.S. Patent 807,491—in which he proposes to pass the gases escaping from the main furnace into a second apparatus, in which they are exposed to electrical action in order to ozonise the atmospheric oxygen. It is alleged that the ozone reacts according to the equations,

$$NO + NO_2 \rightarrow N_2O_3,$$
$$N_2O_3 + 2O_3 = N_2O_5 + 2O_2$$
$$N_2O_5 + H_2O = 2HNO_3,$$

and that absorption is thus greatly facilitated.

The numerous patents which deal with the absorption of the nitrous gases and so forth will be partly discussed later (German Patents 180,691, 313,338; Austrian Patent 27,722). In German Patents 244,840 and 246,712 the proposal is made to interpose a sulphuric acid tower behind the ordinary acid absorption towers. The nitro-sulphuric acid so formed is to be utilised for preliminary drying of the reaction gases before they enter the oxidising tower.

J. Moscicki, whose joint activities with Professor Kowalski, of Freiburg, Switzerland, have already been referred to (U.S. Patent 754,147/1904), described a new type of furnace for the production of nitric acid in 1905 (German Patents 198,240, 209,959, 236,882, 252,271, 265,834; French Patent 380,614; Swiss Patent 38,044. etc.). We will give a short description of the type illustrated in Fig. 54. The central electrode a is situated at sparking distance from the electrode b. Inert gases, such as steam or cooled reaction gases already loaded with NO, are blown through the electrode a by the tube h and then expand in the form of a cone.

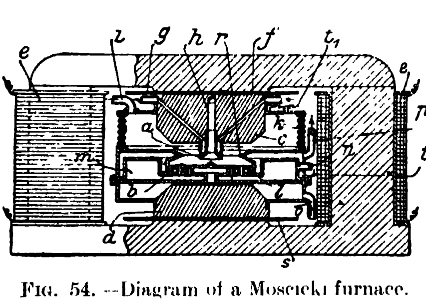


FIG. 54.—Diagram of a Moscicki furnace.

The electric arc maintained between a and b rotates under the influence of a magnetic field in the immediate neighbourhood of the flat electrode b; short circuiting is prevented by the cone-shaped gas current passing through from h. The gases to be oxidised enter the plant at i. In German Patent 230,170 Moscicki

proposes to absorb the product in a tower in a mixture of sulphuric acid of 60° to 61° Bé. and 60 per cent. nitric acid. The gases escaping at the top of the tower, which are saturated with HNO_3, are absorbed in a second tower, in which pure nitric acid is obtained. In a third tower the remaining quantities of nitrogen oxides are absorbed by washing with dilute nitric acid. At the base of the first tower dilute sulphuric acid escapes, free from nitric acid, and is concentrated by the hot furnace gases in lead pans until it once more attains a concentration of 60° to 61° Bé. This process should be compared with German Patent 147,564, U.S. Patent 751,147, British Patent 2,047/1903, French Patent 339,505, and Swiss Patent 26,993 of the Initiativkomitee für die Herstellung von Stickstoffhaltigen Produkten, Freiburg, Switzerland. Moscicki has studied the absorption of nitrous gases in detail, and the result of his investigations will be more closely considered below (German Patent 256,295; U.S. Patent 1,046,212).

In 1908 the Neuhausener Gesellschaft für Aluminiumindustrie approached Moscicki with a view to the acquisition of his oxidation and absorption processes for their plant at Chippis. Moscicki first demonstrated the whole process in his 60-h.p. experimental furnace, after which an agreement was concluded in August, 1908. In the first instance 2,500 cu. m. of furnace gases, containing 2 to 2·5 per cent. of NO, had to be treated hourly at Chippis (Valais) (French Patent 403,401; British Patent 8,958/1908; Swiss Patents 45,636 and 45,637). Absorption was then carried out entirely in 8 scrubbing towers of about 1·5 m. diameter and 6 m. high, through which the gases passed after being cooled and oxidised in interposed oxidation towers. The tower acid contained 40 per cent. of HNO_3.

After overcoming certain difficulties, the towers worked satisfactorily, but at the end of 1909 the escaping gases still contained 0·3 per cent. of NO. When the plant was enlarged, absorption chambers were added (French Patent 444,027; British Patent 17,355/1911; Swiss Patent 58,406).

The second Moscicki plant at Bory-Jaworzno, Poland, was still under construction in 1921. It is designed to utilise 7,000 kw. for the manufacture of concentrated nitric acid and ammonium nitrate. The furnaces correspond to those described in German Patent 265,834.

Having described the Birkeland-Eyde, Schönherr, Pauling, Rothe, Siebert and Moscicki systems, we have exhausted those processes of atmospheric nitric acid manufacture which are now used on a large technical scale. During the last few years, however, the process of the Norwegian inventor, Wielgolaski, which has already been referred to in the economic section, has been operated on

the west coast of the United States. We have still to discuss numerous patents and other publications which also deal with the problem.

In the *Zeitsch. f. Elektrochem.*, **25**, 255 *et seq.* (1919) H. Andriessen published an article on the technical utilisation of atmospheric nitrogen by means of the electric arc,[1] to which we must first refer. His interesting theoretical speculations led him to the conclusion that on theoretical grounds high yields should be favoured by making the proportion between the surface of reaction over which the arc extends during one period as small as possible relatively to the energy evolved by the arc. Further it is desirable to extend the length of the alternate current arc during each current fluctuation as far as possible by magnetic influences, in order to increase the terminal voltage of the arc after ignition, and so to suppress its short-circuiting action, in order to obtain useful electrical working conditions. These two conditions are contradictory, for an arc can only be drawn out to a great length by a magnetic field if a large space is available for its extension. But when comparing two arcs magnetically extended over a given area, that one is best suited for the combustion of nitrogen in which the proportion of linear extension to the reaction area is the greatest.

H. Andriessen (partly in association with J. Scheidemandel) has described the following arrangement for the purpose (German Patents 284,341, 285,111 and 296,395): The arc which plays between electrodes *ab* and *cd* (Fig. 55) and lies in a plane *gh* parallel to the magnetic field, is distorted to traverse a sharply curved path by a mechanical blast. Air is injected through the jet *c*, and deflects the arc forming two limbs, *bf* and *cf*. The arc which has been so deflected is further expanded by the magnetic field to cover an extensive area, *bfc*, bounded by the spiral, *ikl*. By suitable adjustment of the air current and other factors, it is possible to approach the electrodes *b* and *c* so closely that the pitch of the spiral limiting the extension of the arc amounts to a few millimetres only, by which means the whole arc may be confined to an astonishingly narrow space. In an arc

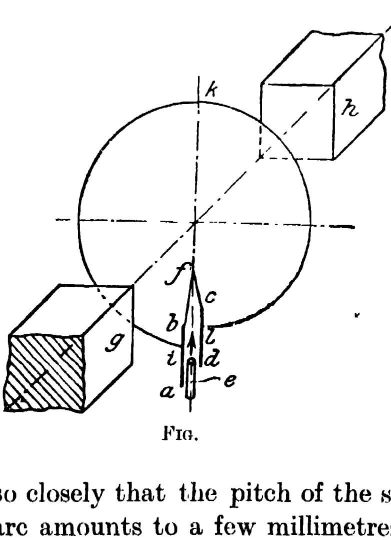


FIG.

[1] *Bulletin des Schweiz Elektrotechn. Vereins*, November, 1918, vol. xi., No. 11.

consuming 8 kw. an expansion of 40 cm. was obtained with an interval between the electrodes of 10 mm.

The number of patents dealing with this matter is so large that it is impossible to discuss them all in detail. We will therefore confine ourselves to an enumeration of the most important, which are : F. de Marc (German Patent 174,177), Société Anonyme d'Électricité et d'Automobiles Mors, of Paris (German Patent 180,290), A. de Montlaur (German Patent 188,750), A. Hauck (German Patent 193,518), F. H. Loring (German Patent 196,113), A. Gorboff and V. Mitkeritsch (German Patent 196,114), K. Hichle (German Patent 200,006), M. Plaatsch (German Patent 200,138), E. Marquardt and C. Warth (German Patent 200,332), G. Kettler (German Patents 205,538, 209,961), F. Spitzer (German Patent 210,324), E. J. du Pont (U.S. Patents 943,661, 950,703), D. Timar (German Patent 223,887), Le Nitrogéne, Geneva (German Patents 228,423, 262,874), P. Bunet, A. Badin and the Comp. des Produits Chimiques d'Alais, etc. (German Patent 237,796), C. P. Steinmetz (U.S. Patents 894,547, 904,071, 904,072, 904,073), A. Wielgolaski (Norwegian Patent 20,328 ; German Patents 258,052, 270,758, 272,853) ; A. Mahlke (British Patent 24,296/1906), Ferranti (Swiss Patent 40,978), A. Scherbius (German Patents 213,709, 221,129), R. Pawlikowski (German Patent 225,195), H. Howard (U.S. Patent 952,248), Bridge (U.S. Patents 832,767, 832,768), F. H. Krebs (German Patent 250,684), R. von Koch (German Patents 249,946, 261,102, 262,920, 265,166, 276,841 ; Danish Patent 16,733 , French Patent 451,361), L. Roberts (U.S. Patent 906,607), W. Kochmann (German Patents 260,134, 263,652), etc.

Haber's experimental investigations, already referred to on the specific electric action of the high-tension arc, were applied to the development of a process using a cooled electric arc, embodied in British Patent 15,490/1908 and German Patent 210,166.

German Patents 199,561 and 206,948 of the Electrochemischen Werke G.m.b.H., of Berlin, deal with the use of a mobile high-tension arc ; in German Patent 212,881, Kunheim & Co., of Berlin, claim the production of an arc unaccompanied by an aureole (decomposition zone) which is alleged to be particularly suitable for promoting endothermic gaseous reactions. In German Patent 205,774 and Swiss Patents 31,189 and 37,037 the same firm publishes further interesting details of its process. German Patent 211,196 of the Zentralstelle für wissenschaftlichtechnische Untersuchungen G.m.b.H., of Neubabelsberg, deals with the construction of a furnace for the production of long, continuously burning arcs which do not need extension by means of an air current or a magnetic field. German Patent 202,400 of the Aluminium Industrie A.G., Neuhausen, deals essentially with

an arrangement of connections for several small arcs. In German Patent 210,821, A. A. Naville, Ph. A. Guye, and Ch. E. Guye claim an alternate current arc rotated by means of a three-phase field of differing frequency from the arc itself (see also German Patent 225,153 and Austrian Patents 34,567 and 34,568). Dynamit A.G. vorm. Alfred Nobel & Co., Hamburg, in their German Patents 211,196 223,366, 228,849, 242,210, 252,270, claim the production of long stable arcs, similar to those of the B.A.S.F., produced inside a tube with special safety precautions. German Patents 228,422, 234,591 and 235,429 of the Chemische Fabrik Griesheim-Elektron claim approximately horizontal arcs and the rapid removal of the reaction products. According to German Patent 228,755 and French Patent 386,171 of H. Albihn, the lines of force of the magnetic field are shortened and very uniformly distributed. According to German Patent 230,042 of K. Kaiser, Wilmersdorf, small amounts of ammonia are mixed with the air. According to German Patents 200,876 and 194,326 of the Westdeutschen Thomasphosphatwerke, Berlin, the air is heated to 1,000° C. before being passed into the furnace or is mixed with explosive substances. In German Patents 183,041 and 183,597 A. I. Petersson, Alby, Sweden, describes an electric furnace in which an arc plays from a central electrode to a ring-shaped or screw-shaped counter-electrode surrounding the former and revolving under the influence of a magnetic field. The process is described in a more extended form in German Patent 202,605 and U.S. Patents 880,037 and 880,464. Each electrode is traversed by an independently generated electric current, and in this way the velocity of the main arc is greatly increased. Forked electrodes are used by the Société Anonyme d'études elektrochimiques, Geneva (German Patent 187,585). We must also refer to patents by D. Helbig (German Patents 189,864 and 225,239).

The Elektrochemische Werke G.m.b.H., Berlin, directed by Werner Siebert, have patented a process for the treatment of gases by means of moving arcs (German Patents 206,948, 259,815 and 268,410). A furnace for operating this process is described in detail in German Patent 266,117 by Elektrochemische Werke and F. Rothe.[1] The furnace casing b (Fig. 56) is of considerable cross-section, whilst its height and width are small; g_1 and g_2 are the gas inlets and e_1 to e_3 the electrodes. The air traverses a spiral track to the exits f_1 and f_2. By this process it is possible to confine large quantities of power in a single disc-shaped arc. In German Patent 268,410 a furnace is described in which the gas can be rapidly chilled in such a manner that the concentration of nitric oxide rises to 2·5 per cent.

[1] Ullmann's "Encyclopædia," vol. ix (1921), pp. 654 *et seq.*

(German Patent 316,349). Other forms of furnace are described in German Patent 262,830 of E. Wassmer; German Patent 266,345 and French Patent 443,620 of F. Russ and V. Ehrlich; German Patent 267,003 and French Patent 449,817 of W. S. Lee; British Patents 14,871 and 886/1913 of E. K. Scott; British Patent 804/1912 of E. Guye; British Patent 919/1912 of H. Grohmann; German Patent 267,871 of J. Simpson Island; German Patent 279,309 of J. du Pont; and German Patent 279,461 of A. Foss. A furnace patented by A. Helffenstein of Vienna (German Patent 262,325) is presumably intended mainly for the arc synthesis of hydrocyanic acid. In French Patent 455,530 E. Rossi proposes to use zinc or aluminium electrodes, as it is stated that in this case the arc flame is particularly rich in electrons. According to German Patent 321,287 electrodes of silicon or of aluminium silicide are still better.

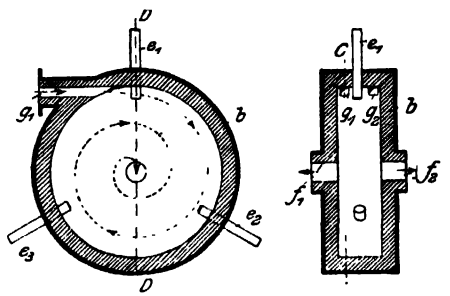


FIG. 56.

According to German Patent 294,200 of A. G. Brown Boveri & Cie. electric arcs are magnetically influenced in evacuated receivers. German Patent 317,137 deals with a method of leading the current to an arc furnace by means of a electrode situated on the hearth. In German Patent 297,773 A. Maschke describes a process of producing a disc-shaped arc by the introduction of air or gas in a suitable manner. According to German Patents 298,846 and 316,214 R. Mewes suddenly chills the hot compressed reaction gases by the addition of pre-cooled or liquefied air, and expands the gaseous mixture with production of external work in order to utilise its energy of expansion. The Bergmann Elektrizitätswerke A.G. varies the air quantity introduced into the furnace chamber in synchronism with the periodicity of the alternating current supplying the furnace; a synchronous motor adjusts a valve built into the air mains (German Patent 298,952). In German Patent 300,722 K. Friedrich describes the production of a disc-shaped arc from a vertical arc burning downwards. According to German Patent 303,152 F. C. Ucar starts the arc by the oscillation of a high-tension current, which is produced in an auxiliary circuit. In German Patent 303,073 A. v. Lipinski describes a furnace with a magnetically extended arc. The mining company Georg. von Giesches Erben have patented the production of a disc arc by the impact of two gas streams

carrying the arc (German Patents 297,773, 310,270 and 311,456). German Patent 314,884 of the Gesellschaft für Elektrostahlanlagen m.b.H. and W. Rodenhauser deals with electrode holders for electric arc furnaces. German Patent 317,502 of H. Spiel deals with the production of an arc between the surface of a liquid and a tube-shaped electrode. German Patent 321,307 of the Maschinenbau-Anstalt Humboldt describes an electrode holder, as does also German Patent 321,308.

E. K. Scott (British Patent 4,725/1913) describes the advantages of his three-phase furnace [1] (Kilburn-Scott three-phase furnace); 15 per cent. of power is saved by utilisation of the steam from a boiler. The yield is increased by 20 per cent. by injecting into the furnace equal volumes of oxygen and nitrogen instead of ordinary air. The theoretical yield increases from 819 to 1,850 kg. per kilowatt year or by 125 per cent. if the temperature of the arc is raised from 3,200° to 4,200° C., that is, by 30 per cent. W. T. Hoofnagle [2] passes the air through a drying chamber before combustion. It then passes into an expansion chamber and enters the cylindrical reaction furnace at reduced pressure (U.S. Patent 1,169,824). It is here subjected to high-tension alternating current of low current density. The current is started and stopped automatically according to the momentary pressure. The pressure is in turn regulated by the formation or decomposition of the higher nitrogen oxides. The reaction chamber is followed by the absorption arrangement and finally by a vacuum pump. A combination of various processes is also claimed in British Patent 1,820/1914.

It has already been mentioned that for many years the action of the electric arc was supposed to be of a purely thermal character, until Haber's investigations altered this view. It is therefore understandable that attempts were soon made to combine nitrogen and oxygen to nitric oxide in ordinary explosion flames. According to German Patents 192,883, 217,079, 217,550, 227,490, 258,925, 277,435, 279,007 and British Patent 8,653/1907, O. Bender burns air with superheated steam in an oxy-hydrogen flame, cools the reaction gases with relatively cold steam, and claims to obtain a yield of 2·9 per cent. of nitric oxide in the combustion gases. At a later period Bender used numerous small flames of a gas containing carbon or hydrogen and water gas as a heating agent. Finally, he adds a water spray to the combustion gases of an ordinary furnace in the proportion of 1 kg. of water to 1 kg. of carbon burnt, and this water is

[1] *J. Soc. Chem. Ind.*, **34**, 113 (1915); *Chem. Met. Eng.*, **19**, 710, etc. (1918); *Chem. Ztg.*, 1916, "Repertorium," p. 348; *Zeitsch. f. angew. Chem.*, 1918, ii., 125, 395.
[2] *Chem. Met. Eng.*, **14**, 342 (1916).

decomposed to a considerable extent, particularly at increased pressure, with formation of compounds of nitrogen and oxygen and of nitrogen and hydrogen. If the products are stabilised by sudden chilling—for example, by a grid through which water is circulated—about 100 gms. of fixed nitrogen are obtained per kilogram of carbon in the fuel.[1] When the temperature is 2,000° C. within the furnace, a mixture of carbon dioxide, nitrogen and oxygen with 1 per cent. by volume of NO and 0·25 per cent. of NH_3 is obtained, and the two latter components rapidly combine with formation of ammonium nitrite. H. Brünler and H. Kettler maintain flames below the surface of water (French Patents 363,617, 363,618 and 380,467) or inject a mixture of nitrogen, oxygen and fuel gas under pressure through numerous jets into a spherical reaction chamber, within which an intensively white-hot ball of flame is formed (German Patents 185,094, 205,351, 209,961 ; British Patents 5,852/1906, 5,901/1906). K. Baron von Vietinghoff-Scheel produces nitrous gases by burning a combustible containing carbon or hydrogen in a mixture of nitrogen and oxygen whilst injecting a finely divided substance of catalytic activity, such as the dust of fluorspar (German Patent 222,629). A process of production of nitric acid from nitrogen tetroxide, oxygen and water is alleged to operate more favourably if the components are caused to interact under pressure (German Patents 225,706). According to German Patent 219,494 of the B.A.S.F., needle-shaped flames of carbon monoxide are used, in order to remove the reaction products rapidly. According to R. P. Pictet (German Patent 226,867) the production of nitrous oxide, N_2O, may be attained from a flame fed with oxygen and nitrogen by means of a temperature fall. According to German Patent 229,142 of H. O. Pfennigsche Erben, Berlin, NO is formed by combustion of a completely gasified fuel with superheated oxygen in slotted burners under pressure. We must also refer to German Patents 171,623, 230,863 and British Patent 26,728/1905 of R. Pawlikowski ; German Patent 182,297 of the Westdeutsche Thomasphosphatwerke G.m.b.H., Berlin (dealing with the interaction of air and of oxy-hydrogen gas in a thin-walled porous porcelain tube) ; U.S. Patents 773,407 and 817,082 of E. Mitchell and D. Parks ; U.S. Patent 758,774 of G. Pauling ; and Norwegian Patent application 23,201 of K. Södermann.

The most important of all similar processes are those described by F. Häusser[2] (British Patents 12,401/1906, 13,989/1907 ; German Patents 216,518, 281,813 and 232,569), who obtains nitrogen oxides

[1] As in many other cases, the translator wishes to dissociate himself from any responsibility for the accuracy of these statements.—TRANSLATOR.

[2] *Verhandl. d. Ver. z. Beförd. d. Gewerbefleisses*, 1905, p. 295 ; *Stahl u. Eisen*, 1921, Nos. 28/29.

in a combustion engine or a bomb by suddenly cooling the reaction products by means of a spray, so that the reversed reaction can no longer take place. The heat of the compressed gases can be utilised for the production of mechanical work. The energy lost by spraying at the maximum temperature must be considered as work required for the production of the nitric acid which is obtained. If the cooling occurs over a short but fairly high temperature range, it may be calculated that fairly good yields should be obtained theoretically by this process. According to E. R. Besemfelder,[1] yields of 120 to 150 gm. of nitric acid per kilowatt hour have been obtained by this process in continuous thoroughly controlled experiments.

O. Dobbelstein [2] has discussed the Häusser process in detail, and Häusser himself has given further details in his article on "Neue Versuche über die Stickstoffverbrennung in explodierenden Gasgemischen" [3] ("New Experiments on the Combustion of Nitrogen in exploding Gaseous Mixtures"). The experiments described by Dobbelstein were carried out atthe Nürnberg Works of the Maschinenfabrik Augsburg-Nürnberg, on behalf of the Deutsche Stickstoffindustrie G.m.b.H., lighting gas only being used. This was aspirated and compressed to 4 atm. Air was compressed to 6 atm. in a second compressor after oxygen had been added to increase the yield. This was pre-heated in a furnace fed with producer gas and then entered the explosion bomb of a capacity of 100 litres, where the air and illuminating gas were mixed. The escaping gases, containing nitric oxide, passed through a cooling coil into an oxidising tower in which NO_2 was formed. A proper absorption train was not originally provided, and the gases were therefore expelled through a small final tower. The explosion caused an increase of pressure, during one-tenth of a second, to 8·5 to 23 kg. per square centimetre ; this was maintained during about 0·15 second, and in a further quarter of a second the explosion was ended. The explosion and expulsion of the product together occupied a time of half a second only. Dobbelstein gives an estimate of the cost of a plant for the treatment of 500,000 cu. m. of coke-oven gas per twenty-four hours.

On the basis of the results obtained at Nürnberg an experimental works was erected in 1913 at the de Wendel Colliery, near Hamm, Westphalia (Stickstoffwerke Herringen A.G.) for the treatment of coke-oven gas in two explosion bombs, each of a capacity of 100 litres. When the bomb was first operated a difficulty was encountered above

[1] *Chem. Ztg.*, 1918, p. 404.
[2] *Glückauf*, 1912, pp. 289–300.
[3] *Mitteilungen über Forschungsarbeiten*, 1913, part 133.

a certain pressure, which had never occurred during the Nürnberg trials at much higher pressures and explosion temperatures, even during many days' working ; it was found that the explosive mixture ignited immediately on entering the bomb, a phenomenon similar to the well-known pre-ignition in gas engines. Whilst, however, it is known that there is an explanation in the latter case, namely pre-ignition by glowing oil residues and so on in the cylinder, the occurrence in the bomb could not be explained in this way, as the interior was always free from residues of any kind. These difficulties were very serious, and much work was necessary to overcome them to such an extent that continuous working could be maintained. The exit valves of the bombs, through which the reaction product escapes at the full explosion pressure and high temperature of the explosion, did not at first prove suitable for continuous working. Ultimately, however, a valve construction was devised which worked satisfactorily.

The bombs worked at a compression of 5½ to 6 atm., an explosion pressure of about 25 atm. and 40 to 45 explosions per minute. The air for the combustion was passed in counter-current through the hot explosion gases, and was pre-heated to about 300° C. The installation worked day and night with purified coke-oven gas of 3,600 to 4,200 nett cals. per litre. It was found unnecessary to add additional oxygen as had originally been intended.

The concentration of nitric oxide in the explosion gases corresponded to the Nürnberg results with lighting gas of 0·45 volumes per cent. ; after removing the water of combustion, which could be effected without appreciable loss of the nitric oxide, a 28 per cent. acid was obtained. Absorption was carried out in a system of scrubbing towers, together with special oxidation chambers. The arrangement proved quite satisfactory.

Early in 1918 the 100-litre bombs were replaced by a bomb of 300 litres capacity, which worked under the same conditions. The results were favourable ; 44 to 45 explosions occurred per minute, and the gases contained 18·5 gm. of HNO_3 per cubic metre. The yield of nitric oxide was much higher than before, being 0·6 to 0·7 per cent. of NO by volume in the waste gases. The yield of HNO_3 was 96 to 107 gm. per cubic metre of coke-oven gas of a calorific value of 4,000 cals. per cubic metre.

In his lecture before the German Chemical Society on the "Combination of Elementary Nitrogen with Oxygen and Hydrogen," F. Haber [1] also communicated various data on the formation of nitric

[1] *Chem. Ztg.*, 1913, pp. 584–585.

oxide in flames under pressure. This led to a lively controversy [1] between him and F. Häusser.

According to German Patents 281,084 and 281,525, E. Herman burns methane in air enriched with oxygen, preferably at 20 to 30 atm. pressure, using zirconia as a catalyst. The combustion gases are said to contain 3 to 4 per cent. by volume of NO. German Patent 305,124 describes flameless combustion in presence of aluminium nitride. According to German Patent 289,844, W. Lachmann passes nitrogen and oxygen over magnesia heated to a high temperature. F. R. Gerhardt (German Patents 303,255 and 321,981) and R. Ibach (German Patent 305,130 and U.S. Patent 1,122,932) claim special improvements in internal combustion engines in order to attain the high temperatures necessary for the oxidation of nitrogen. According to a patent of H. Nöh (German Patent 306,451), in order to increase the nitric oxide yield in four-cycle explosion engines, the oxidised

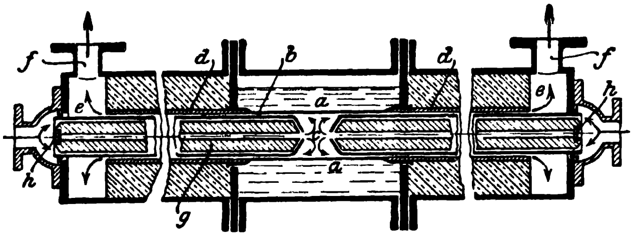


FIG. 57.

gases are scavenged by air. According to German Patent 314,948 of the Gewerkschaft des Steinkohlenbergwerks Lothringen, Gerthe-i.-W., and M. Kelting, a process and apparatus are claimed for the combustion of nitrogen. By the impact of two equal gas currents a disc of flame is obtained which is cooled at its extreme circumference by oils, molten salts or alloys. Two gas mains *b*, of fire-proof material, which are contracted to jets at *c*, meet at that point in the centre of the water-cooled metallic tube *a* (Fig. 57). Tubes *d* of fire-proof material fit tightly into the prolongations of the outer tube and are well insulated. These lead into flues *e* for the combustion gases, provided with exit ports *f*. The interiors of tubes *b* are provided with cores *g*, which force the gases along the outer walls. The jets *c* can be observed through sight-glasses *h*. Fuel gas and air or other oxygen and nitrogen carriers are introduced through the tubes *b*—for example, fuel gas along the one tube and air along the other. The gases are highly heated during their passage through the annular channel from *b* to *g* by the action of the effluent gases passing from

[1] *Chem. Ztg.*, 1913, pp. 635, 771, 769; see also "Repertorium," 1913, p. 111; 1914, p. 586.

b to *d*; whilst very hot they meet at the exits of the jets *c* to form a disc-shaped flame, offering a large surface, and out of contact with the walls.

The combustion gases flow radially outwards and divide into two currents, which traverse the two tubes *b* in the direction of the flues *e*, being rapidly cooled to about 1,500° C. in the space between *a* and *b*. During their passage from *b* to *d* they impart the larger portion of their heat to the entering gases in *b*.

This furnace unites the principle of a disc arc with the methods used for ordinary combustible gases. The Gewerkschaft Lothringen is pursuing investigations along these lines, as is clear from a series of patent applications—for example, German Patents 324,264, 325,635, 325,800, 326,228, and others.

J. Görlinger utilises mixtures of coal gas and producer gas for driving gas engines for the production of nitric oxide, according to German Patent 316,253. In order to attain the necessary turbulence for the production of nitric oxide in two-cycle gas engines, the fuel gas is led into the cylinder at the commencement of the stroke, whilst finely compressed air is added in a rapid jet at a later stage (German Patent 316,677). The oxy-acetylene flame produces more nitrogen oxides than any other similar flame. Ozone has also been observed in this flame. More than 4 parts of nitric oxide are formed per 100 parts of carbon dioxide in the combustion gases.[1] M. Krause (German Patent 318,963) uses the effluent gases from internal combustion engines for heating purposes after reinforcing them with steam. Explosion flames are also used by W. Franklin and the General Electric Company, according to U.S. Patent 1,064,064. We may also mention German Patent 245,492 by W. A. Phillipps. Details on the production of nitric acid from the combustion gases from gas engines are given by Sorg in *Metallbörse*, 1921, p. 356.

If bauxite is heated by the introduction under pressure of an explosive mixture into its pores, for example of a mixture of air and lighting gas, it is dehydrated and sintered until its volume is diminished by half. Its porosity remains quite unimpaired; 50 litres of a gaseous mixture can be burnt in one second in 2,000 c.c. of bauxite. The product is cooled by steadily injecting air whilst gradually diminishing and finally cutting off the supply of combustible gas. The product which is obtained is as active as platinum, and its activity is in direct proportion to the contents of Al_2O_3. According to German Patent 322,843 and French Patent 472,959 by N. Lecesne, if, for example, a mixture of bauxite and carbon is burnt in air only, 400 gm. of nitric acid are obtained per kilogram of fuel. According

[1] J. H. Vogel, "Das Acetylen," Leipzig, 1911, p. 32.

to British Patent 131,609/1916 of C. J. Montgomery and E. R. Royston, fuel gases are burnt in the cylinder of a gas engine with the help of a catalyst.

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(*a*) Combustion in the arc is dealt with by C. Rossi, Nitrum A.G., Norsk Hydro, Kilburn-Scott, L'Azote Français, Lummer, Maye, Mewes, Real, and others, in German Patents 321,287, 329,179, 331,040, 300,722, 330,079, 298,846, 304,372, 356,413 ; Swiss Patents 89,232, 89,715, 88,554, 88,906, 90,692, 88,379 ; Austrian Patent 82,759 ; British Patents 163,026/1920, 166,095/1920, 134,229/1919 ; French Patents 534,998, 523,353 (addition 23,245), 518,737, 524,121 (addition 23,637), 524,636 ; Norwegian Patent 28,762 ; U.S. Patents 1,368,019, 1,429,013. These patents deal with furnace construction, electrodes, the action of catalysts, and the effect of bases, such as Al_2O_3, ZnO_2. Fe_2O_3, bauxite, CaO, MgO, etc., during the absorption of the dilute primary gases, addition compounds of which yield more concentrated gases by secondary decomposition (*Ber.*, **54**, 1776 (1921) ; *Annalen*, **424**, 71 (1921) ; see also *Transactions of American Electro-chemical Society*, **34**, 221 (1922) ; *Chem. and Met. Eng.*, **22**, 299 (1920)).

The recovery of waste heat, etc., is dealt with in Norwegian Patent 32,770 ; U.S. Patents 1,379,260, 1,420,477, and German Patent 337,795, which deals with nitrous oxide.

Analytical matters are dealt with in *Jour. Ind. Eng. Chem.*, **14**, 308 (1922), and calculations in *Chem. Trade Journal*, **68**, 170 (1921).

(*b*) Non-electrical methods of combustion in internal combustion engines, four-phase motors, regenerative furnaces, etc., are dealt with in Austrian Patent 88,574 of F. Gerhardt ; German Patents 303,255, 321,981, 351,286 ; 324,264, 325,635, 325,800, 326,228, 329,846/7, 331,488 by Gewerkschaft Lothringen and M. Kelting ; German Patents 309,154, 338,940 ; U.S. Patent 1,408,754. The most detailed work is that concerned with the process of F. Häusser (*Stahl u. Eisen*, **41**, 195 (1921) ; *Jour. Soc. Chem. Ind.*, **41**, 253 (1922)).

CHAPTER XXV

The Catalytic Oxidation of Ammonia to Nitric Acid

WHEREAS the direct synthetic production of nitric acid from the air has so far been of importance in those countries only which dispose of large water powers, the catalytic oxidation of ammonia plays a much more important part. Germany obtained practically the whole of the enormous quantity of nitric acid which was required for the War from 1914 to 1918 by this means, for the one arc process plant at Rhina-i.-B. made practically no difference. According to an article by the Italian, Giovanni Morselli, which was cited and abstracted in the *Chemical Trade Journal and Chemical Engineer* of September 7th, 1918, the daily German production of nitric acid and ammonium nitrate for war purposes during 1918 was 1,000 tons. According to this article the German production of nitric acid in 1915 was already 10,000 tons, and the total amount spent on the erection of German nitrogen works was 400,000,000 marks.

A valuable critical study of the catalytic oxidation of ammonia, in which the early history of the process is referred to, was published by B. Neumann and H. Rose.[1] The earliest production of nitric oxide by such means was probably carried out by Fourcroy about the year 1800 ; Fourcroy exploded a mixture of ammonia with excess of oxygen in a red-hot tube. The origin of the modern method of catalytic oxidation may be traced to the French chemist, Kuhlmann, in 1839, who worked in presence of platinum at above 300° C. and suggested the technical application of the reaction. Schönbein and Liebig [2] used ferric oxide for the same purpose.

Kuhlmann's experiments were completely forgotten in course of time, but the subject was revived by W. Ostwald in 1900. Ostwald was unable to obtain a patent in Germany on account of the priority of Kuhlmann's work on the oxidation of ammonia over platinum, but his process was successfully patented in Switzerland (No. 25,881), in England (Nos. 698/1902, 8,300/1902), in U.S.A. (No. 858,904), in France (No. 317,544), in Austria (No. 37,136), and in other countries. Ostwald pointed out that platinum promotes the oxidation of ammonia to nitric oxide, higher oxides and nitric acid, and that a second reaction takes place simultaneously which results in the production

[1] *Zeitsch. f. angew. Chem.*, 1920, i., 41, 45, 51.
[2] *Mag. d. Pharm.*, **33**, 40 ; *Journ. f. prakt. Chem.*, **70**, 129 (1856).

of free nitrogen. At a red heat and at a high velocity a mixture of air and ammonia containing 10 or more parts of air to one part of ammonia is mainly oxidised to nitric acid in the presence of metallic platinum, partially or entirely coated with a layer of platinum sponge or platinum black. On the other hand finely divided platinum favours decomposition with production of nitrogen. With a platinum contact 2 cm. long a gas velocity of 1 to 5 m. per second is required. The quantity of oxygen should not be less than corresponds to the equation :—

$$2NH_3 + 7O = 2NO_2 + 3H_2O.$$

The most favourable temperature is between a dull and a red heat, and is certainly above 300° C. The gas velocity should be so adjusted that the time of contact between the platinum and the gas is not longer than one-hundredth of a second. It is advisable to pre-heat the gaseous mixture. The process has been described in detail by W. Ostwald, O. Schmidt and R. Böcker, N. Caro and others.[1] According to Ostwald's British patent, the apparatus consists essentially of two concentric tubes forming an effective counter-current unit. The outer tube is of brass, enamelled internally, and has a diameter of 4 inches. The inner reaction tube is constructed of nickel and is $2\frac{1}{2}$ inches in diameter. The gaseous mixture traverses the outer tube first (Fig. 58) and is pre-heated by the inner nickel tube in which the reaction takes place. The top of the nickel tube is furnished with the platinum contact cylinder consisting of platinum wire which is wound on a carrier. The most suitable reaction temperature is slightly below 600° C. Nickel and quartz are found to be the only resistant materials which do not seriously promote decomposition of the ammonia. At 500° C., however, nickel already promotes this decomposition appreciably. Aluminium is better in this respect, but unfortunately has but little resistance to temperature influences.

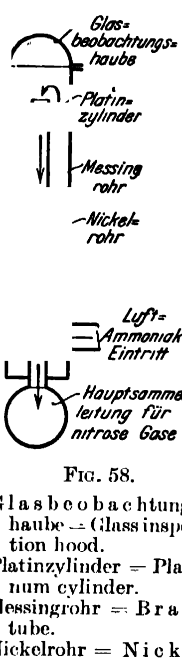

FIG. 58.

Glasbeobachtungshaube = Glass inspection hood.
Platinzylinder = Platinum cylinder.
Messingrohr = Brass tube.
Nickelrohr = Nickel tube.
Luft-Ammoniak-Eintritt = Inlet for air and ammonia.
Hauptsammelleitung fur nitrose Gase = Collecting main for nitrous gases.

As a catalyst Ostwald recommends platinum partly covered with platinum sponge, palladium, iridium, rhodium, chromium, man-

[1] *Chem. Ztg.*, 1903, p. 457 ; *Berg. u. hüttenmänn. Rundschau*, 1906, p. 71 ; *Ber.*, **39**, 1366 (1906) ; *Zeitsch. f. angew. Chem.*, 1904, pp. 1713 and 1909.

ganese dioxide, lead peroxide, the oxides of nickel, chromium, iron, copper, silver and so forth. The best results have been obtained with platinum covered with platinum sponge and at a red heat just discernible in daylight. The products are absorbed in the usual manner. In Austrian Patent 37,136, Ostwald describes a form of catalyst in detail. In this the catalyst zone consists of approximately parallel metal plates forming channels at an angle with the direction of the gas current and which completely occupy the cross section of the reaction chamber. As a constructional material, nickel steel may be used (German Patent 207,254) or aluminium (Swiss Patent 41,262), at least for those portions which do not come into contact with condensed nitric acid.

W. Ostwald has developed his system in detail jointly with E. Brauer [1] since 1900. Owing to the refusal of the German Patent Office to grant a patent, the patentees were forced to treat their process as a secret process in Germany. The first technical experiments commenced in 1901 on the property of the Zentralstelle für wissenschaftlich-technische Untersuchungen Neubabelsberg at Königswusterhausen. Other work was carried out in 1905 at the Gewerkschaft des Steinkohlenbergwerks (Zeche) Lothingen at Gerthe (near Bochum), Westphalia. The first large installation was started at Gerthe in 1908, and treated coke-oven ammonia. In 1910 a further large plant was erected at Vilvorde in Belgium by the predecessors of the Nitrogen Products and Carbide Company, and started operation in 1912. In this plant cyanamide ammonia was used for the first time. Ostwald and Brauer also erected and operated a special experimental plant for the Chemische Fabrik Griesheim-Elektron. Details of the process in its laboratory stage were also communicated to the Höchster Farbwerke. Detailed plans with all constructional details were also supplied to the Berlin Anhaltische Maschinenbau A.G., the representative of which firm studied the plant at Gerthe for several days. Finally certain information was supplied to interested parties in France and the United States, who also inspected the Gerthe plant during erection and operation.

In spite of all attempts to introduce the process, it was declined everywhere at that time. The reason for this was that the difference in price between nitrogen in the forms of ammonia and of nitric acid was at that time too small. In Germany the Lothringen Colliery was alone able to place the process on a financially sound basis by using its own coke-oven ammonia. The fact that other considerations, such as those of national defence, might render the development of this important process desirable, was not appreciated by administrative

[1] Private communication.

and technical leaders before the War, in spite of many publications by Ostwald.[1]

The Gerthe installation was considerably enlarged during the War and used as a model for other plants. Ostwald and Brauer however, took no part in the large-scale development of their ideas.

An anonymous author reports on the process in detail. He describes a plant for the conversion of 25 tons of ammonia gas per month into 150 tons of nitric acid of 36° Bé., which had been working for six years (Gerthe). On passing the gases slowly over the platinum contact, only a small percentage yield is obtained, whilst almost theoretical yields are obtained on passing them through rapidly. The process is worked at 300° C., and the contact period is small (1/100 second) in order to avoid the decomposition of the ammonia to nitrogen and hydrogen ; rather more oxygen is used than corresponds to the equation :—

$$2NH_3 + 7O = 2NO_2 + 3H_2O.$$

The ammonia must be free from carbon dioxide and hydrogen sulphide, and must therefore be purified by milk of lime ; it is then mixed with air and passed into the catalyst unit. This consists of cast iron, and of stoneware beyond the point at which nitric acid condenses. The oxidised gases pass into 5 cooling towers lined with stoneware. The dilute scrubber acid is continually circulated through the towers by pumping ; in the second tower it attains a strength of 36° Bé. 30 catalyst units, each containing 50 gm. of platinum, supply 200 kg. of 53 per cent. acid daily ; the depreciation amounts to 1·5 gm. per day per unit. After four to six weeks the platinum must be removed and sold as waste metal. Regarding details of the cost of plant and of manufacture for the production of both nitric acid and ammonium nitrate, we must refer to the article itself.[2] In 1917 the Lothringen Colliery treated about 600 cu. m. of ammoniacal liquor of 16 to 18 per cent. by the Ostwald process. Concentrated aqueous ammonia is distilled in columns with stirrers in a current of steam with the addition of milk of lime ; in this way a sludge of calcium carbonate and calcium sulphide is obtained, together with almost pure ammonia gas. The final traces of hydrogen sulphide are removed by means of pure concentrated ammonia solution. The ammonia is collected in gas holders, mixed with air in the proportion of 1 to 10, and then passed over the contacts. These consist of vertical tubes about 3 m. high.

To each battery of contacts there are attached 9 vertical Steuler towers standing in the open, of which 8 are acid towers,

[1] *E.g., Zeitsch. d. ver. Deutsch. Ing.*, 1903 ; *Berg. u. hüttenmänn. Rundschau*, 1907.
[2] *Chem. Ztg.*, 1913, "Repertorium," p. 553.

whilst the ninth is scrubbed with alkaline liquor. The combustion gases are cooled from 400° to 80°–90° C. in flat rectangular coolers constructed of "V2A" metal, over which water trickles. The Steuler towers are about 15 m. high and about 5 m. in diameter. At the end of 1917 there were 3 series, each of 9 towers.

The tower acid is neutralised with ammonia or alkali in vats provided with stirrers and ammonium or sodium nitrate is obtained by evaporation and crystallisation. A portion of the acid is concentrated by sulphuric acid.

The calcium sulphide waste liquors from the distilling columns are treated with carbon dioxide in scrubbers; hydrogen sulphide is evolved, which is converted into sulphur in Claus ovens; 4 to 5 tons of sulphur are thus obtained daily.

The maximum output capacity of the Gerthe plant during the War is said to have been 170 tons of sodium nitrate, 230 tons of ammonium nitrate, or 200 tons of concentrated nitric acid per twenty-four hours. The working conditions have now, of course, been completely altered.

Schmidt and Böcker [1] obtained a yield of about 80 per cent. of nitrous acid alone with a platinum contact. On the large scale the total yield of nitrogen oxides with Ostwald contacts may be 80 to 90 per cent.

Nothing further has been heard of the Ostwald plant which was to have been erected at the vorm. Erzherzoglich Friedrichsche Werke in former Austrian Silesia immediately after the first results were known. The works at Vilvorde,[1] in Belgium, were unsuccessful owing to the quality of the ammonia, and ceased operations entirely in consequence of the War. The English works at Dagenham met with such difficulties in obtaining raw material that they never were in regular operation, and the French works at Angouleme alone gave satisfactory results. After thousands of tons of cyanamide ammonia had been converted into nitric acid by the Ostwald elements, symptoms of poisoning suddenly occurred in the catalyst, which reduced its activity very greatly, and were due to phosphorus compounds. In order to remedy this difficulty, those decomposition gases which contained phosphine were specially released from the cyanamide autoclaves [2]; the yield then increased considerably.

Apart from the above information and the information published in book form by W. Kochmann [3] and by E. Donath and A. Indra,[4]

[1] *Iron and Coal Trades Review*, May 23rd, 1913.
[2] Ch. L. Parsons, *J. Ind. Eng. Chem.*, **11**, 541 (1919).
[3] "Deutscher Salpeter" (Berlin, 1913).
[4] "Die Oxydation des Ammoniaks zu HNO_3" (Stuttgart, 1913).

Wehrheim,[1] Reinhers, Cats,[2] Menegini,[3] Wenger and Urfer,[4] and N. Smith [5] have published theoretical and laboratory investigations on this subject.

Neumann and Rose [6] deal with all the above literature on the oxidation of ammonia in their article, in which they also publish a series of important experimental results. They heat a vertical quartz tube in an electric resistance furnace. A narrow quartz tube is introduced through a rubber stopper at the lower end of the larger tube; this serves to introduce the gas and extends into the middle of the furnace. When platinum is used as a contact material, it is introduced in the form of fine platinum gauze placed in the expanded upper end of the reaction tube; when oxides are used as catalysts, the tube is expanded above into a beaker-shaped extension 9 cm. long and 1 cm. in diameter, in which the catalyst is placed.

Neumann and Rose use liquid ammonia from a cylinder, wash the gas with ammoniacal copper solution in order to remove any acetylene, and simultaneously aspirate air, which is measured by a gas meter, through the apparatus. The gases are mixed in a horizontal tube 47 cm. long and 3 cm. wide, which is charged with glass wool and caustic soda and holds 360 c.c. of gas. The mixtures ordinarily contain 7 to 8 per cent. of ammonia.

The reaction products are most conveniently absorbed by two tubes charged with sulphuric acid of sp. gr. 1·84. Nitric oxide alone is hardly soluble in sulphuric acid, but in presence of oxygen nitrogen trioxide is formed, which combines with the sulphuric acid to form nitrosyl sulphuric acid:—

$$N_2O_3 + 2H_2SO_4 = 2HSO_3NO_2 + H_2O.$$

One cubic centimetre of sulphuric acid of sp. gr. 1·84 absorbs at least 55·34 mg. of nitrogen trioxide. Nitrogen dioxide also forms nitrosylsulphuric acid without any coloration of the sulphuric acid:—

$$2NO_2 + H_2SO_4 = HSO_3NO_2 + HNO_3.$$

At the ordinary temperature the dioxide is a mixture of 20 parts of NO_2 and 80 parts of N_2O_4; at 64° C. the two components are present in equal proportions, whilst at 150° C. nitrogen dioxide molecules alone are present, which decompose completely at 620° C., forming $NO + O$.

The nitric oxide contents of the sulphuric acid which has been

[1] "Dissertation" (Darmstadt, 1910).
[2] *Chem. Weekblad*, **9**, 47 (1912).
[3] *Gazz. Ital.*, **42**, 8, 126 (1912); **43**, i., 81 (1913).
[4] *Ann. Chim. appl.*, **23**, 97 (1918).
[5] *Proceed. Chem. Soc.*, **22**, 39 (1906).
[6] *Loc. cit.*; *Zeitsch. f. angew. Chem*, 1920, i., 41 *et seq.*

used for absorption are determined in a Lunge nitrometer. By direct titration of a portion with N/10 permanganate solution the nitrous acid is determined. In order to determine the unconverted ammonia, 10 to 20 c.c. of the absorption acid are shaken with mercury in order to remove all the nitric oxide, and the acid is then carefully neutralised with cooling and a little sodium sulphide added, after which it is distilled with caustic soda and the ammonia absorbed in N/10 sulphuric acid.

Ammonia burns in air under the influence of a catalyst, and forms in the first instance a white fog of ammonium nitrite and ammonium nitrate, but, starting at about 300° C., reddish-brown vapours appear, and with rising temperature more and more free nitrogen and steam are formed. The main reactions which occur are the following :—

(1) $4NH_3 + 5O_2 = 4NO + 6H_2O + 215{\cdot}6$ cals.
(2) $2NH_3 + 3O_2 = 2HNO_2 + 2H_2O + 153{\cdot}7$ cals. (solution).
(3) $NH_3 + 2O_2 = HNO_3 + H_2O + 80{\cdot}9$ cals. ($95{\cdot}3$ cals. in solution).
(4) $4NH_3 + 3O_2 = 2N_2 + 6H_2O + 302$ cals.
(5) $4NH_3 + 7O_2 = 4NO_2 + 6H_2O + 269{\cdot}5$ cals.
(6) $4NH_3 + 6NO = 5N_2 + 6H_2O + 431{\cdot}6$ cals.

When a considerable length of catalyst is traversed by the gases reaction (4) predominates. Thus the thickness of the contact layer and the velocity of the gas current are very important factors in ensuring satisfactory oxidation. If in the above reactions pure oxygen is replaced by air, the resulting mixture may contain a maximum of 14·38 per cent. by volume of ammonia only, according to equation (1) ; 12·28 per cent., according to equation (2) ; 9·50 per cent., according to equation (3) ; 21·87 per cent., according to equation (4); and 10·72 per cent., according to equation (5). Starting from a mixture of ammonia and air and operating to obtain nitric oxide, according to equation (1), 14 per cent. of ammonia is the highest practically permissible proportion ; if nitric acid is to be produced, then the gases should contain not more than 9 per cent. of ammonia. When pure oxygen is used, the results are usually worse ; the temperature often rises in an uncontrollable manner, much free nitrogen is formed, and explosions may even occur.

The first reaction product is naturally nitric oxide. Even when the resultant products are rapidly absorbed, the nitric oxide combines with oxygen to form nitrogen trioxide, and a small proportion forms the dioxide. According to Neumann and Rose, 90 per cent. of the oxidation products consist of nitrous acid when burning ammonia in air. When oxygen is used for the oxidation more nitric

acid is formed, whilst the proportion of nitrous acid amounts to 20 to 30 per cent. only. From the commencement, reaction (4) occurs together with the others; the extent to which it occurs increases with rise of temperature, and also if the quantities of catalyst used are too large, or if the gas velocity is too low. Dissociation of nitric oxide scarcely occurs, and only becomes noticeable at 700° C., proceeding very slowly even at that temperature. Reaction (6) is, however, very important, as it already occurs at temperatures at which the formation of nitric oxide commences. The reaction

$$NH_4NO_2 = N_2 + 2H_2O + 718 \text{ cals.}$$

also gives rise to the formation of nitrogen at low temperatures, and thus reduces the yield of nitric oxide. All the above reactions are exothermic and cause a rapid rise of temperature as soon as one or the other of them has started.

Ostwald had already shown that when oxidising ammonia it is advisable to pass the gaseous mixture as rapidly as possible over the catalyst, and that for each catalyst there is a definite velocity at which a maximum yield is obtainable. Neumann and Rose use a platinum gauze with 3,000 meshes per square centimetre, which is also used in technical practice, and pass through this a mixture of ammonia and air containing on the average 6·3 per cent. by volume of ammonia at 450° C., using a catalyst area of 3·32 sq. cm. in an experimental furnace. Their results are given in the following table :—

Litres of air per hour, at normal temperature and pressure.	NH_3 per hour.	Percentage yield of NO.
7·80	0·633	62·69
8·86	0·689	64·51
11·30	0·891	76·36
16·86	1·050	91·22
19·80	1·267	96 06
23·09	1·738	95·80
26·98	1·721	93·10
31·62	1·991	90·40

In the light of these results, which are supported by those obtained in practice, the results of Andersen [1] are quite inexplicable.

We have already referred to the influence on the yield of nitric oxide of the proportion of ammonia in the mixture. According to equation (4), $NH_3 + 5O_2 = 4NO + 6H_2O$, not more than 14·38

[1] *Zeitsch. f. Elektrochem.*, 1916, p. 441.

per cent. of ammonia should be used when mixed with air; whilst according to Ostwald's equation, $4NH_3 + 7O_2 = 4NO_2 + 6H_2O$, only 10·74 per cent. of ammonia should be employed. If we assume the production of nitrous or nitric acid, according to the above equations (2) and (3), the highest percentages of ammonia should be 9·53 and 12·28 per cent. respectively. The results of Neumann and Rose mostly refer to 7 to 9 per cent. of ammonia in air. Other circumstances being equal, the yield of nitric oxide falls with increased concentration of ammonia, being 98·73 per cent. with 3·22 per cent. of ammonia, 96·06 per cent. with 6·00 per cent. of ammonia, and 93·10 per cent. with 8·65 per cent. of ammonia. With a satisfactory catalyst, however, this effect is less apparent. Up to 9 per cent. by volume of ammonia, the yield is always more than 90 per cent. over platinum gauze.

Contrary to many previous statements, Neumann and Rose found the optimum temperature with a platinum gauze to be about 500° C. The reaction starts at 300° C., being characterised by the appearance of a white fog of ammonium nitrite or nitrate. In consequence of the exothermic character of the reaction the temperature rises rapidly, characteristic reddish-brown vapours appear, and at 350° C. the reaction is already fairly vigorous. The following table shows the result with a uniform velocity of the gas current, and about 9·5 per cent. by volume of ammonia in the mixture, when passed over 3·3 sq. cm. area of platinum gauze :—

Furnace temperature.	Percentage yield of NO.	Decomposed NH_3 (per cent.).	Nitrogen (per cent.).
350° C.	60·25	17·72	22·03
400° ,,	84·66	3·43	11·91
450° ,,	93·10	1·08	5·82
550° ,,	92·65	—	7·35
625° ,,	81·66	—	18·34
730° ,,	71·89	—	28·11

The reaction velocity increases very rapidly between 300° and 400° C. At 500° C. the yield of nitric oxide attains a maximum with 91·73 per cent.; above 450° C. no more free ammonia occurs. The first occurrence of free nitrogen is due to the decomposition of ammonium nitrite :—

$$NH_4NO_2 = N_2 + 2H_2O.$$

As the temperature rises the following reaction occurs :—

$$4NH_3 + 6NO = 5N_2 + 6H_2O;$$

whilst above 500° C. the formation of free nitrogen is mainly due to the oxidation of ammonia, according to the equation :—

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O.$$

Neumann and Rose compare their results with those of other investigators in the following table :—

Neumann and Rose. Platinum gauze		Wehrheim. Platinum foil.		Reinders and Cats. Platinum asbestos		Wenger and Urfer. Platinum asbestos with oxygen.		Meneghini. Platinum spiral.	
	Per cent		Per cent.		Per cent.		Per cent.		Per cent
300° C.	—	300° C.	18.00	—	—	357° C.	54·5	350°	3·7
400° C.	60·25	350° C.	28·36	—	—	396° C.	80·1	405°	7·6
450° C.	93·10	375° C.	39·86	—	—	450° C.	91·9	430°	15·0
500° C.	95·73	400° C.	50·85	—	—	533° C.	97·6	450°	24·7
550° C.	92·65	425° C.	72·52	—	—	562° C.	97·7	475°	34·7
625° C.	81·66	450° C.	80·77	510° C.	59·6	610° C.	91·7	515°	45·1
730° C.	71·89	—	—	590° C.	79·7			550°	58·2
	—	—	—	660° C.	80·8			610°	64·4
		—	—	—	—			680°	66·1

The fate of the ammonia can be accurately followed by investigation of the products absorbed by sulphuric acid. The results are as follows :—

	350° C.	400° C.	450° C.	500° C.	600° C.	700° C.
	Per cent	Per cent.	Per cent.	Per cent.	Per cent	Per cent.
As NH_3	17·72	3·43	1·08	—	—	—
,, N_2O_3	54·37	76·50	87·12	89	81	68·55
,, NO_2	5·88	8·16	5·98	7	8	8·50
,, N_2	22·03	11·91	5·82	4	11	23·00

Of the total nitrogen oxides, 93 to 97 per cent. are almost invariably found as nitrous acid, and 3 to 7 per cent. only as nitric acid. This result is confirmed by those of other workers. Much larger yields of nitric acid can be obtained by working with pure oxygen only (1 volume of ammonia to 2 of oxygen) and a platinum asbestos catalyst ; under these conditions at 562° C. and with 97·7 per cent. total yield, the proportion of nitric acid may rise to 75·4 per cent., whilst that of nitrous acid is 22·3 per cent.

Neumann and Rose utilised the data obtained by them on the combustion of ammonia over platinum gauze to produce the accompanying curves (Fig. 59).

If, instead of absorbing the reaction gases immediately behind the furnace, as in obtaining the above figures, time is allowed for oxidation before they are absorbed, the proportion of nitrogen dioxide, and therefore of nitric acid, rapidly increases at the expense of the nitrogen trioxide, owing to the action of oxygen.

The observation that the oxidation of ammonia is catalytically accelerated by the presence of iron oxide is due to Schönbein and Liebig. Neumann and Rose precipitate ferric hydroxide from a

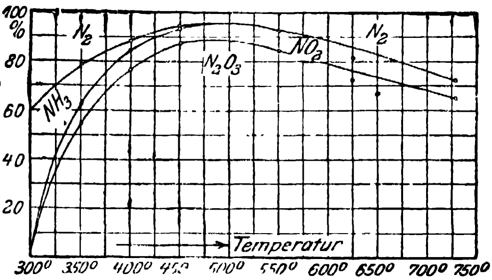

FIG. 59.

solution of ferric chloride with ammonia, wash and form the pasty mass into small spheres, which they dry and ignite. They obtained the following figures with an average gas velocity of 22 litres per hour and a mixture containing about 9·35 per cent. by volume of ammonia :—

Furnace Temperature.	NO yield per cent.	Undecomposed NH_3 per cent.	N_2 per cent.
440° C.	47·5	—	—
505° ,,	69·1	11·5	19·3
550° ,,	73·0	7·2	19·8
670° ,,	89·9	Trace	10·1
715° ,,	84·5	*Nil.*	15·5
755° ,,	83·5	,,	16·5
820° ,,	77·3	,,	22·7
865° ,,	59·3	,,	44·7

The most favourable reaction temperature is 670° to 700° C., at which a yield of nitric oxide of 90 per cent. is obtained. The fate of the ammonia which is used is as follows, in volumes per cent. :—

	500° C.	600° C.	700° C.	800° C.
NH_3	11·7	3	—	—
N_2O_3 . . .	57·4	78	83	70
NO_2	11·7	9	5	9
N_2	19·2	10	11	21

From these figures the curves (Fig. 60) have been constructed for the combustion of ammonia over iron oxide.

In order to control the statements of German Patent 293,824 of the B.A.S.F., experiments were carried out with a mixture of iron oxide and 3 to 4 per cent. of bismuth oxide. With gas velocities of

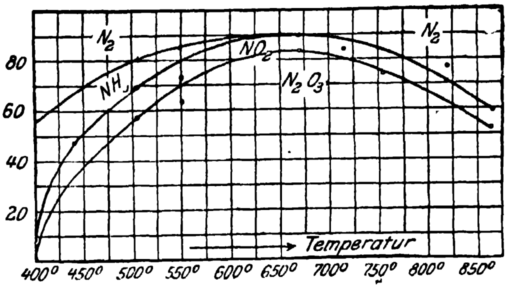

FIG. 60.

22 to 23 litres per hour and ammonia concentrations of 9·2 per cent. by volume, the following figures were obtained :—

Furnace Temperature.	NO yield per cent.	Undecomposed NH_3 per cent.	N_2 per cent.
500° C.	87·7	6·24	6·1
550° ,,	94·4	1·76	3·8
600° ,,	94·9	*Nil.*	5·1
650° ,,	92·0	,,	8·0
720° ,,	91·5	,,	8·5
760° ,,	88·3	,,	11·7
815° ,,	84·4	,,	15·6

A maximum yield of about 95 per cent. is obtained at 550° to 600° C., as compared with 700° C. with iron oxide only, and 500° with

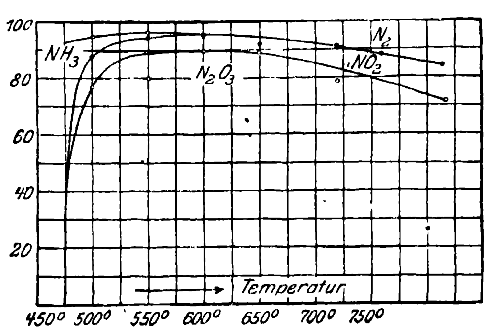

FIG. 61.

platinum ; the maximum yield with iron oxide is 90 per cent. Below 480° C. no nitric oxide is formed, but from that temperature upwards

the reaction velocity rises rapidly. The curve (Fig. 61) is based on the following results :—

Fate of the NH_3 in Volumes per cent.

	500° C.	600° C.	700° C.	800° C.
NH_3 . . .	6·24	—	—	—
N_2O_3 . .	76·76	89·54	85	74
NO_2 . . .	10·94	5·36	8	12
N_2 . . .	6·06	5·10	7	14

With other catalysts greatly diminished yields are obtained ; iron oxide mixed with 3 to 4 per cent. of copper oxide gives a maximum yield of 53 per cent. NO at 550° C. ; burnt pyrites, 46 per cent. at 770° C. ; iron oxide with 3 to 4 per cent. of cerium oxide, 37 per cent. at 610° C. ; and iron oxide with 3 to 4 per cent. of thorium oxide, 52 per cent. at 585° C. According to Neumann and Rose, chromium oxide on pumice shows a maximum yield of 49·6 per cent. at 658° C., whilst 6·39 per cent. of NH_3 are undecomposed and 43·98 per cent. are converted into free nitrogen. With vanadium oxide a maximum yield of 17·9 per cent. of nitric oxide is obtained at 540° C., whereas at 630° C. 88·9 per cent. of the ammonia is destroyed with formation of free nitrogen. Copper oxide is a bad catalyst, as is shown by the following maximum figures which were obtained :—

Air, in litres per hour.	Per cent. of NH_3 in the mixture by volume.	Furnace temperature.	NH_3 in litres per hour.	Yield of NO.	Undecomposed NH_3.	Decomposed with formation of nitrogen.
				Per cent.	Per cent.	Per cent.
22·34	9·05	800° C.	2·44	24·1	47·1	28·8

From the above figures the theoretical thermal conditions of the reactions may be calculated. Neumann and Rose made this calculation in the case of a platinum catalyst at 500° C. The reaction gases still contained 5·6 per cent. of free oxygen. Thus, theoretically the maximum quantity of NH_3 in the entering gases which can be oxidised is 12·55 per cent. In practice this upper limit can never be attained. The reaction temperature itself is calculated to be 782° C. when the entering gases contain 9 per cent. by volume of NH_3. In the case of platinum this temperature is actually far too high. The system should, therefore, properly be cooled. The fact that this is unnecessary in manufacturing practice is due to radiation losses from the metallic portions of the plant. Works

control should not, therefore, be confined to the adjustment of the mixture of air and ammonia before entering the catalyst chambers, but should be extended to temperature control.

When the mixture contains 6 per cent. of NH_3, a temperature of 534° C. only should theoretically be obtained. Allowing for the radiation losses, which would represent a temperature reduction of 150° to 200° C., it is apparent that such a mixture can no longer be oxidised with a maximum yield without external heating.

It is not found necessary to heat the catalyst in ordinary technical practice. The heat of reaction suffices to maintain the oxidation after the contact has once been heated to a sufficiently high temperature to start the reaction. If the concentration of the ammonia is more than 9 per cent., it is rather a case of cooling than of heating. In general the temperatures employed in practice are too high. The average yield with a platinum gauze catalyst is 90 to 95 per cent.

When working with an iron oxide catalyst a temperature of 700° to 800° C. is maintained and yields of 80 to 85 per cent. are attained

Jul. Baumann [1] has investigated the thermo-chemistry of the oxidation of ammonia by considering the two limiting reactions :—

$$(1)\ 2NH_3 + O_5 = 2NO + 3H_2O\ ;\ \text{and}$$
$$(2)\ 2NH_3 + O_3 = N_2 + 3H_2O.$$

When starting from a mixture of 1 cu. m. of ammonia and 8 cu. m. of air, at about 800° C., over platinum in an industrial unit, an excess of heat of 1·27 cals. is obtained according to equation (1) per molecule of ammonia—that is, the gaseous mixture will continuously react without external heating if there are no radiation losses and the proper reaction temperature has once been attained. According to equation (2), 20·1 cals. are produced per molecule of NH_3. If the catalyst becomes excessively hot on the large scale this is due to reaction (2) ; thus, in this case, the ammonia molecule is being destroyed with the formation of free nitrogen and steam. In this case the hydrogen flame, burning in a confined space, sometimes gives rise to the acoustic phenomenon of "singing." When the yields are poor, the singing of the apparatus is therefore often very noticeable.

The difference in the temperatures of 500° C. given by Neumann and Rose and 800° C. by Baumann is very noticeable. It is partly explained by the character of the gases which were used. In their laboratory experiments Neumann and Rose used liquefied ammonia from a cylinder. The mixture obtained by their methods of working will be almost absolutely dry. On the large scale—and J. Baumann was concerned with manufacturing conditions—it is

[1] *Chem. Ztg.*, 1920, p. 145 ; see also *Chem. Zentralbl.*, 1920, iv., 707.

to be noted that the ammonia as obtained from the plant is saturated with water vapour, and that the air from the intake is also moist, also that the ammonia gas used is never so pure as that from a cylinder. The presence of water vapour hinders the decomposition of the ammonia, and therefore permits a higher combustion temperature to be used without serious decomposition and formation of nitrogen. The ordinary impurities of technical ammonia, such as carbon dioxide, also favour a temperature rise during oxidation. We will consider later the poisoning effect caused by various of these impurities. It should, moreover, be noted that laboratory experiments usually yield more favourable results than those on a continuous commercial scale.

We have already referred to the work of Wenger and Urfer on the oxidation of ammonia with the help of a platinum or rhodium catalyst.[1] F. C. G. Müller has also contributed interesting work on the formation of free hydrogen in the "reversed" ammonia flame.[2] E. Schlumberger and W. Piotrowski established the fact that mixtures of ammonia and air may act as explosives between the limits of 16·5 and 26·8 per cent. of NH_3 by volume.[3]

Important contributions to the subject of the oxidation of ammonia have been supplied by E. B. Maxted.[4] W. G. Adam[5] describes the experiments on ammonia oxidation carried out by C. Davis in the laboratories of the Gas, Light and Coke Company at Beckton in the years 1908 and 1909, as a result of which an installation for the production of 1 ton of nitric acid daily with a platinum gauze catalyst was erected in 1917.

The work of J. R. Partington[6] is of great interest; his apparatus comprised conically shaped upper and lower portions between which three rectangular prismatic portions are interposed. The individual parts are interconnected by $\frac{3}{4}$-inch flanges, and the whole arrangement resembles the well-known Bamag-Frank-Caro ammonia combustion unit. The upper section holds the catalyst, whilst the three lower sections contain baffle-plates. The conical hoods are provided with mica-covered sight holes of 1·5 inch diameter. The whole apparatus (converter) consists of aluminium castings. The walls are 0·2 inch thick, and the prismatic central portions measure 4 by 6 inches. The gas delivery and outlet tubes are of thick aluminium tubing of 2-inch bore. The whole converter is 4 feet long and weighs about 32 lb. Thorough mixing of the air

[1] See also *Zeitsch. f. angew. Chem.*, 1918, ii., 395.
[2] *Ibid.*, 1920, i., 24.
[3] *Zeitsch. f. komprim. u. fluss. Gase*, **7**, 49 (1915).
[4] *J. Soc. Chem. Ind.*, **36**, 177 (1917).
[5] *Chem. Trade Journ.*, **62**, 181 (1918).
[6] *J. Soc. Chem. Ind.*, **37**, 337 (1918); *Chem. Zentralbl.*, 1919, ii., 909.

and ammonia is the most necessary requirement in working. Partington recommends that 25 per cent. ammonia solution should be trickled down a coke tower into which air is injected below, together with a little steam. The gases are cooled in the upper portions of the tower, whilst the steam is condensed. In order to remove all dust particles, particularly iron oxide; the gases are filtered through coke or glass wool. The catalyst consists of one or more layers of platinum gauze ; the gauze is of 80 mesh, and the diameter of the wire is 0·0025 inch ; it is fixed in an aluminium frame.

The oxidising reaction, $4NH_3 + 5O_2 = 4NO + 6H_2O + 220$ cals., requires to be initiated by electrically pre-heating the catalyst gauze. This may equally well be pre-heated by a non-luminous coal gas flame. The heat of reaction then maintains the gauze at a red heat. It must be replaced after about three months. The yield of nitric oxide mainly depends on the number of layers of gauze, on continuous electrical heating of the catalyst, and on pre-heating the gaseous mixture or the air to about 350° C. before it enters the oxidising unit ; also on the proportion of air to ammonia. The above described plant, which is intended for sulphur'c acid works, is large enough for a plant producing 80 tons of sulphuric acid daily, and produces 1·5 tons of nitric acid (HNO_3) per square foot of catalyst surface in twenty-four hours, with an average yield of 95 per cent. when working continuously. The gauze weighs about 50 gm. per square foot. When two layers of gauze are used, as much as 15 kg. of nitric acid are produced daily per gramme of platinum. The reaction gases have a temperature of 400° to 600° C. They are cooled to 30° C. and converted into nitrogen dioxide by means of air. They contain about 10 per cent. by volume of nitrogen oxides, and may either be led directly into the lead chambers or condensed to nitric acid.

G. A. Perley [1] contributes an important bibliography and considers the theory of the reaction in detail. He recommends that in general several layers of gauze, of 0·0026 inch wire, should be used, and says that it is advisable to mix the warm air with the ammonia just before they reach the catalyst. The most prejudicial impurities are naphthalene vapour, tar, phosphorus compounds, and so forth.

O. Dieffenbach [2] has discussed the economics of the conversion of ammonia into nitric acid or ammonium nitrate by means of a combination of the arc and cyanamide ammonia industries. Although the position has altered completely since May 15th, 1914, when Dieffenbach's article was written, many of his main conclusions are

[1] *J. Ind. Eng. Chem.*, **12**, 5, 119 (1920).
[2] *Chem. Ind.*, 1914, pp. 265 *et seq.*

undoubtedly still correct. E. Donath [1] developed Dieffenbach's conclusions still further and applied them to the Häusser process.

We can only mention here in passing that ammonia may also be oxidised by electro-chemical means.[2] Liquid ammonia reacts with ozone with complete decomposition of the latter, according to the equation :—[3]

$$2NH_3 + 3O_3 = NH_4NO_2 + 3O_2 + H_2O, \text{ and}$$
$$2NH_3 + 4O_3 = NH_4NO_3 + 4O_2 + H_2O.$$

In the United States a specially constructed ammonia oxidation unit has been developed, in which platinum is always used as a catalyst and which we will discuss later. F. G. Liljenroth [4] in particular has described the process.

The platinum which is employed should always be as pure as possible. The presence of iridium and palladium only is allowable, whilst 0·02 per cent. of iron has an injurious effect. The platinum must not be treated in iron vessels. For the same reason iron gas mains may also act injuriously. It is advisable to wash the surface of the platinum with hydrochloric acid.

Three qualities of platinum gauze were tried, namely :—

70 mesh	of 0·0026-inch	diameter.	
80 ,,	0·0026	,,	,,
100 ,,	0·0015	,,	,,

The 80-mesh quality proved to be the best. It was found that smooth platinum wire acts indifferently, if at all, and that the surface must first be activated. After pre-treatment during several hours in air containing much ammonia at 800° C. the surface of the wire becomes rough and is no longer bright, but has a grey appearance and an almost spongy surface. Liljenroth illustrates the structure of the contact surface by very instructive micro-photographs.[5] He finds that the most favourable temperature for continuous working on the large scale is about 825° C. The temperature of the platinum should not exceed 900° to 925° C. and should never fall below 750° C. If the temperature of the gauze is maintained by the heat of reaction the most suitable proportion of ammonia in the gaseous mixture is 10 to 12·5 per cent. by volume ; if the catalyst is heated electrically not more than 10 per cent. by volume should be present. The pre-heaters for the gases must be constructed of aluminium, as otherwise the decomposition of ammonia into its elements is greatly accelerated.

[1] *Loc. cit.*, p. 513.
[2] *Chem. Ztg.*, 1915, "Repertorium," p. 203.
[3] *Ibid.*, 1920, p. 758.
[4] *Chem. Met. Eng.*, **19**, 208 (1918).
[5] See also Parsons, *J. Ind. Eng. Chem.*, **11**, 541–552, Figs. 10 to 12.

This decomposition has been studied by the following, amongst others: W. Ramsay and S. Young,[1] E. P. Perman and G. A. S. Atkinson,[2] A. H. White and W. Melville.[3] Recent experiments by G. B. Taylor and others led to the following values:—

Catalysts.	Temperature.	Percentage of NH_3 destroyed.
Pure aluminium cuttings	550° C.	0·0
Glazed earthenware fragments	680° ,,	0·8
2 mm. nickel wire	500° ,,	1·4
2 mm. nickel wire	580° ,,	11·3 (1·8 per cent. oxidised to NO)
2 mm. nickel wire	690° ,,	22·0 (1 per cent. oxidised to NO)
Porcelain	700° ,,	0·0
Alundum cement	710° ,,	34·0
Alundum cement	590° ,,	2·3

In the United States the yield obtained in the catalyst unit is determined analytically (G. B. Taylor and J. D. Davis[4]), or by weighing both the ammonia used and the products obtained. With continuous working an average yield of 91 per cent. may be expected; in exceptional cases yields of 95 to 96 per cent. are obtained.

Alvin Allen Campbell[5] has communicated interesting data on the action of platinum gauzes from the laboratory of the Newark Wire Cloth Company, of Newark, N.J. The following table is a summary from his article:—

Mesh per inch.	Diameter of wire in inches.	Active surface in square inches.	Active surface in square inches per gram of platinum.	Weight in grams per square inch.	Air spaces in square inches per square inch of surface.	Surface in square inches per centimetre of platinum.
80	0·0026	1·3873	4·148	0·33815	0·6272	79·9058
80	0·0030	1·5841	3·401	0·46592	0·5774	72·6111
100	0·0026	1·6951	4·013	0·42268	0·5676	88·0941
120	0·0020	1·4748	4·962	0·29863	0·5715	109·0701
150	0·0015	1·4821	7·058	0·21009	0·5990	154·8643
150	0·0020	1·9573	5·243	0·37329	0·4886	115·3401

[1] *J. Chem. Soc.*, **45**, 88 (1884).
[2] *Proc. Roy. Soc.*, **74**, 110 (1904).
[3] *J. Amer. Chem. Soc.*, **27**, 373 (1905).
[4] *J. Ind. Eng. Chem.*, **9**, 1106 (1917).
[5] *Ibid.*, **11**, 468 (1919).

An 80-mesh gauze made of wire of 0·0026-inch diameter has been most used and has proved the most satisfactory. The well-known American expert, Charles N. Parsons, expects still more favourable results with a gauze of 150 mesh, and made of a wire of 0·0015-inch diameter containing 99 per cent. of platinum and 1 per cent. of iridium.

W. S. Landis,[1] who commenced to study the oxidation of ammonia towards the end of 1915 at a time when the entry of the United States into the War began to appear more probable, was entrusted with the conduct of the necessary experiments by the American Cyanamide Company at the commencement of 1916. He considers the reaction to be represented by the two equations :—

$$4NH_3 + 5O_2 = 4NO + 6H_2O, \text{ and}$$
$$4NH_3 + 3O_2 = 2N_2 + 6H_2O.$$

According to his results, the first reaction takes place most satisfactorily in presence of platinum at 750° C., or more generally at about 700° to 800° C., with 9 per cent. of ammonia in the initial mixture, whilst the second reaction takes place quantitatively at 915° C. when 10 per cent. of ammonia is present, when the catalyst is working unsatisfactorily. Landis states that the best temperatures are 665° to 690° C. for a mixture containing 10 per cent. of ammonia, and 550° to 580° C. for a mixture containing 8 per cent.

The thorough purification of the ammonia before oxidation is of extreme importance ; very little has so far been published on this subject, as each works uses different methods and treats its own process as a strict secret. Naturally, Haber ammonia, which is itself the product of a sensitive catalytic reaction, is considerably purer than ammonia from cyanamide or from coke ovens. The remarkable phenomena of deterioration and poisoning of the catalyst were in fact first observed when using coke-oven ammonia, as was only natural, as this was used first.

Jul. Baumann [2] has stated that he was able to detect the abnormal behaviour of cyanamide ammonia, as compared with liquid ammonia from coke ovens, extraordinarily quickly on a small scale. He oxidised both gases under identical conditions with a platinum contact. Absolutely normal results were obtained with coke oven ammonia, but the cyanamide ammonia behaved quite otherwise. The yield, which was at first good, dropped very rapidly. The platinum underwent a remarkable change.

" The microscopical investigation did not show the characteristic

[1] *The Chemical Eng.*, 27, 113 (1919).
[2] *Chem. Ztg.*, 1920, pp. 275-276.

roughening of the surface observed by Ostwald, which accelerates the reaction and tends to reduce the yield by causing an excessive combustion of the ammonia to form water and nitrogen."

Baumann found that the platinum wire was covered with a greyish-white film, which could not have been due to contamination of the oxidising air by flue dust, etc., as it had been very carefully filtered.

After prolonged working, the film gradually became thicker, and the yield of nitric oxide fell steadily. On further investigation the film was found to consist of silica. Silicides are formed in the carbide furnace from the lime and coke, and these remain unchanged by the nitrogenation, or are converted into silicon-nitrogen compounds. When the calcium cyanamide is converted into ammonia these silicides or siliconitrides form silicon hydride, and possibly complex nitrogen-silicon compounds. The volatile compounds accompany the gaseous ammonia, and so cause poisoning of the catalyst through their oxidation to silica. Volatilised liquid ammonia, of a quality which oxidises faultlessly when pure, may be caused to show the above characteristic poisoning effects on the platinum by admixture with small quantities of silicon hydride produced from silicon carbide. The gas may be freed from its silicon contents by intensive washing with alkali hydroxide or lime. Cyanamide ammonia which has been treated in this manner gives a good yield on oxidation.

The Österr. Verein für Chem. u. Metallurg. Produktion of Aussig-a.-E. protected this process by German Patent 276,720, Austrian Patent 68,072/1914, and Hungarian Patent 64,871/1913.

Those impurities of crude ammonia which consist of gaseous phosphorus compounds are far more serious in their effects than the silicon compounds, which are much more easily removed. The phosphorus compounds are formed in the carbide in the same manner as the corresponding silicon compounds. The phosphides also behave similarly on nitrogenation; they are partially unattacked and partially converted into complex calcium-nitrogen-phosphorus compounds. When the cyanamide is decomposed the various hydrides are evolved, probably accompanied by some of similar character to phospham. As crude cyanamide ammonia always contains more or less considerable quantities of acetylene, the phosphorus hydride may exercise a very serious effect by promoting spontaneous combustion and thus causing explosions. Moreover, even traces of volatile phosphorus compounds suffice to poison the platinum catalyst during oxidation. The platinum gauze shows greyish-black spots, which rapidly increase in area and enormously

diminish the yield. In such cases manufacture can only be maintained, unsatisfactorily and for a short period only, by heating the contact artificially.

Many qualities of cyanamide ammonia contain exceedingly large quantities of hydrogen sulphide. This is also a catalyst poison, but can readily be removed by washing with milk of lime. It is almost impossible to state what may be the normal composition of cyanamide ammonia liquor. The main impurities are acetylene, hydrogen sulphide, and silicon and phosphorus compounds; carbonates are seldom detectable in the fresh liquor, as they are removed by the free lime used in the decomposition of the cyanamide. The proportions of the various catalyst poisons not only vary in different works, but also alter in any given plant, on account of small alterations in the manufacture or the quality of the raw materials.

For these reasons, and as the individual works have obviously no motive for publishing the methods of purification evolved with much difficulty, no general guidance can be given as to methods of purifying the gas.

The removal of hydrogen sulphide and of silicon compounds is relatively simple, and is effected by washing the ammonia gas obtained by steam distillation of the crude cyanamide ammonia liquor.

Interesting details have been published, more particularly in America, on the removal of acetylene and of phosphorus compounds from the gas. These impurities are readily detected in ammonia liquor by adding silver nitrate solution; the precipitate of silver acetylide which is formed carries with it the greater portion of the phosphorus. Phosphorus hydride and similar compounds can be determined in the gas by absorption with a solution of bromine in hydrochloric acid; by subsequently adding ammonia in excess and then magnesia mixture, the whole of the phosphorus is precipitated as phosphate. The quantities of phosphorus are almost always very small, but very small traces, as low as 0·01 per cent. of phosphorus hydride, exercise an exceedingly disturbing effect on the yield during continuous working.

We have already briefly referred to the difficulties met with in the Angoulême plant. Ch. L. Parsons [1] recommends the removal of phosphorous gases from cyanamide ammonia by the observance of special precautions, such as thorough aeration at normal pressure when manufacturing the ammoniacal liquor and the filtration of the mixture of air and ammonia through the special charcoal used for gas masks, or animal or wood charcoal. The compounds are

[1] *J. Ind. Eng. Chem.*, **11**, 541 (1919); *Ch. Zentralbl.*, 1920, ii., 128.

oxidised to phosphoric acid and ammonium phosphate is recovered. This method, which was first recommended by J. D. Davis, works very satisfactorily. According to U.S. Patent 1,296,820/1919, W. F. Landis passes a rapid current of air through the cyanamide autoclave and thus oxidises the fixed phosphorus. Other impurities occur in ammoniacal liquor resulting from the distillation of coal.

An ammoniacal liquor of which 100 c.c. consume 50 c.c. of N/10 permanganate yields a gas which oxidises perfectly if the platinum gauze is absolutely free from iron oxide and oil. If, however, the permanganate figure exceeds 200, the temperature of the platinum gauze drops, and the yield also drops, as in the case of phosphorus poisoning. If the gaseous mixture is preheated, the yield of nitric oxide is again slightly increased.

F. G. Liljenroth [1] refers to the work of G. B. Taylor and J. H. Capps [2] on the poisoning action of acetylene, phosphorus, and hydrogen sulphide.

The influence of phosphorus is the most serious ; 2 to 3 parts of phosphorus per 100,000,000 exert a noticeable influence. Hydrogen sulphide, or organic compounds which burn without leaving any residue, exercise but little effect if present in minute traces only ; pure acetylene in small quantities does not exert so great an influence as the technical product, obtained as a by-product in cyanamide manufacture. Cyanogen and prussic acid oxidise similarly to ammonia, forming nitric oxide. Iron oxide, fat, oils, tar, and so forth must be most carefully removed, as otherwise dark spots appear on the platinum gauze, which are accompanied by a poor yield. New gauzes must always be carefully purified and freed from fat by washing with pure benzine or ether. The volatile tar oils are especially injurious in the case of ammoniacal liquor with a high permanganate figure.

W. S. Landis [3] has also contributed to the literature of the purification of cyanamide ammonia. He proved that a given condition of the platinum surface corresponds to a definite composition of the gas, and that a pure gas gave a 10 per cent. smaller yield on oxidation than a crude gas with the same catalyst, which had, so to say, adapted itself to the peculiarities of this crude gas. Any change in the quality of the gas is most prejudicial. Under circumstances ten days to two weeks may elapse before the catalysts adjust themselves to the new gas and are correspondingly activated. A catalyst which works faultlessly with cyanamide ammonia usually

[1] *Chem. Met. Eng.*, **19**, 208 (1918).
[2] *J. Ind. Eng. Chem.*, **10**, 457 (1918) ; **11**, 27 (1919).
[3] *Chem. Eng.*, **27**, 113 (1919).

gives bad results with coke oven ammonia, and *vice versâ*. The self-activation and adaptation of the catalyst surface is accompanied by structural changes which lead to a characteristic appearance for each gaseous mixture.

With regard to the removal of phosphoric impurities, it may be said in general terms that oxidising methods are the easiest; these may take the form of the simple addition of air as recommended by Landis, or of chemical or physical methods. The purification of the air supply by the most careful filtration and control of the iron piping is usually neglected in practice. Paint which may have been applied at some time at hidden points within the main may exert an extremely injurious effect so long as it still retains volatile constituents.

Haber ammonia oxidises much more smoothly. The gases utilised for its manufacture must in themselves of necessity be so pure that it is scarcely possible for by-products to be introduced into the ammonia. Any urea which may be present has hardly any influence. The only impurities which need to be considered are possible particles of oil, tar, and so forth. When iron oxide contacts are used for the oxidation of ammonia they are far less sensitive than platinum contacts. They are only impaired or poisoned by phosphoric, silicic and boric acids. The study of the oxidation of ammonia has considerably enlarged our knowledge of the obscure behaviour of catalysts in general.[1]

The determination of the yield from ammonia oxidation is usually carried out by analytical control of the gases, as recommended, for example, by Jul. Baumann.[2] It is obvious that this method is not satisfactory unless carried out with care; this is also clear from a controversy between K. Kaiser and the Bamag.[3] The analytical control should always be supplemented by comparing the weights of raw materials and products before forming a decisive opinion on an oxidation plant. Careful and regular stocktaking at suitable intervals, which enable the measured quantities of ammonia gas to be compared with the weighed and analysed products, give the most reliable figures. The use of really satisfactory and reliable gas meters is therefore a prime necessity.[4]

The patent literature includes numerous proposals for the improvement of ammonia oxidation plants by the construction of suitable apparatus or the introduction of new catalysts. In German

[1] See also G. Bredig, "Katalyse," in Ullmann's "Encyclopædia," vol. vi. (1919), p. 665, and G. Woker, "Die Katalyse," 2 vols. (Stuttgart, 1910–1915).

[2] *Chem. Ztg.*, 1919, p. 466.

[3] *Ibid.*, 1916, p. 112.

[4] See also *Koppershefte*, 1919, Nos. 6, 7: and *Zeitsch. f. angew. Chem.*, 1919, i., 222

Patent 198,472 and French Patent 362,434 Nordyke and Marmon recommend a spiral tube of platinum; Chem. Fabrik Griesheim-Elektron propose the use of quartz or porcelain as carriers for the platinum.[1] Farbenfabriken vorm. Friedrich Bayer & Co. pass air containing 4 to 5 per cent. by volume of NH_3 over iron oxide at 600° to 750° C. (German Patent 168,272; French Patent 335,229).[2]

In German Patent 280,499 and French Patent 464,237 the B.A.S.F. claim the removal of particles of copper and iron dust from the gases by filtration and the use as far as possible of gas conduits of nickel or nickel alloys. German Patents 282,824, 284,815, 287,009, 298,912, 303,241; U.S. Patents 1,207,706, 1,207,707, and 1,207,708 granted to the B.A.S.F., and their co-patentees deal with the preparation of iron oxide contact masses, with additions of 3 to 4 per cent. of bismuth oxide or rare earth oxides. With such iron oxide-bismuth oxide contacts at 700° C. nitric oxide yields of over 90 per cent. are regularly obtained. Phosphoric, silicic and boric acids act as poisons. The contact materials consist, for example, of cubical lumps prepared from 45 parts of pure iron nitrate and 1 to 2 parts of bismuth nitrate. In German Patent 301,362 of the B.A.S.F. copper oxide contacts are recommended.

In German Patent 224,329 Frank and Caro claim the oxidation of ammonia with a 90 per cent. yield over thorium oxide or a mixture of cerium and thorium oxides at 170° to 200° C. Wendriner[3] uses uranium as a catalyst, whilst Orlow[3] uses copper gauze. Farbwerke vorm. Meister, Lucius and Brüning oxidise 10 to 14·5 per cent. of ammonia gas, mixed with exactly the theoretical proportion of air, over platinised asbestos at 550° to 650° C. The nitric acid can be condensed by cooling, and pure nitrogen ultimately remains (French Patent 453,845, German Patent 286,751). If the mixture to be treated is too rich in ammonia, it must be cooled or diluted with inert gases (German Patent 289,562). Instead of working with mixtures of 12·3 volumes of ammonia and 87·7 volumes of air, it is possible to work with a mixture of 40 volumes of ammonia and 60 volumes of oxygen. This mixture is explosive, but if only half the air necessary for combustion is replaced by oxygen there is no longer any danger of explosion. When working at higher pressures, nitrogen tetroxide is directly obtained in liquid form without refrigeration (German Patent 289,563).

Farbenfabriken vorm. Fr. Bayer & Co. state, in German Patent

[1] Neumann and Rose, *Zeitsch. f. angew. Chem.*, 1920, i., 41, 42.
[2] K. W. Jurisch, *Chem. Ztg.*, 1908, p. 790.
[3] Neumann and Rose, *Zeitsch. anorg. Chem.*, 1920, i. 41–42.

299,643, that the output capacity of the plant and the yield of nitric oxide are dependent on the degree of moisture of the gases; they find that the presence of water vapour is favourable, as it enables the temperature to be more readily adjusted, and this increases the possible output. For example, 2 to 6 volumes of water vapour are added to a mixture of about 8 volumes of ammonia and 92 volumes of air before this enters the oxidising unit. The unit, which oxidised not more than 3,000 kg. of ammonia with a 90 per cent. yield when dry gases were used, now treats 4,000 kg. of NH_3 with a 95 per cent. yield of NO. These observations by the Elberfelder Farbenfabriken are in agreement with the remarkable fact that a contact element, when fed with gaseous ammonia of constant quality, and at the same rate, produced varying yields, according to the height of the barometer, so that the yields altered with the latter. Apparently the true cause of this is not the actual barometric pressure, but the degree of atmospheric moisture which varies with the same. Usually little attention is paid to these circumstances in practice.

U.S. Patent 1,037,261, by C. Jones, A. Morton, N. Terzier, and the Semet Solvay Company, Syracuse, N.Y., claims the use of magnesium sulphate as a catalyst at 700° to 750° C. It is alleged that ammonia mixed with 2 to 2·2 volumes of oxygen is oxidised practically completely to nitrogen oxides.

According to German Patent 292,084, the Verein Chem. Fabriken in Mannheim compresses a mixture of ammonia and air before treatment with the catalyst. For each particular arrangement of the catalyst and of the resistance which the gases have to overcome before entering the combustion unit, there is a definite optimum pressure. It is stated that the yield of nitric oxide is increased to 98 per cent. According to German Patent 298,981, by the Permutit A.G., alumina is used as a catalyst. Tufa or artificial aluminium silicates are recommended in conjunction with compounds of the heavy metals. Alkali chromo-silicates, alkali boro-silicates, alkali silico-tungstates, and alkali silico-vanadates are also alleged to give good results. According to German Patent 300,651, W. Manchot and J. Haas support silver oxide on pumice, reduce it to silver, and use it in this form as a catalyst. In German Patent 302,514 A. Classen recommends chromites, silver chromate or manganese compounds as catalysts. According to German Patent 303,052, A. Maschke heats ammonium sulphate or ammonium bisulphate and passes the decomposition products over a suitable contact when mixed with air; it is stated that mixtures of nitric and sulphuric acids are produced.

According to French Patent 473,618 of the Soc. Générale des Nitrures, the yield of nitric oxide is increased by mixing the reaction products with currents of air, nitrogen, and so forth, immediately behind the oxidation unit. In U.S. Patents 1,206,062, 1,206,063 and 1,217,247 Washburn recommends that a small amount of ammonia should be left in the reaction gas mixture in order to prevent the decomposition of the nitrogen oxides. In U.S. Patent 1,193,798 Landis states that a mixture of 1 volume of ammonia with 7·5 volumes of air is the most favourable. When the volume relationship of ammonia to air is 1 to 10 he finds it necessary to heat externally, or to raise the oxygen content of the air to 30 per cent. (U.S. Patent 1,242,958). According to U.S. Patents 1,193,796 and 1,193,797, the mixture of air and ammonia is first passed through a preliminary contact heated to 500° C., the heat evolved in which is removed whilst the resulting mixture is then led into the actual combustion element. The first unit oxidises such impurities as phosphorus and silicon hydrides. The contrivances for adjusting the temperature are described in the patent specification, and sketches are included (see also U.S. Patent 1,120,960).

According to German Patent 280,966, by O. Bender, ammonium nitrite is produced by treatment of active mixtures of nitrogen and oxygen with water.[1] In German Patent 274,346 C. Nordon claims a very original process by which he proposes to obtain nitric acid from moorland soil electrolytically.

Fr. Uhde [2] publishes manufacturing data of the plant at Zeche Lothringen. In 1914 an Ostwald oxidation plant for the manufacture of 10,000 tons of 63 per cent. nitric acid per annum, corresponding to approximately 1,625 tons of NH_3 or 1,338 tons of ammoniacal nitrogen, cost £22,500. The working expenses for wages, overhead charges and repairs without amortisation, amounted to about £3,300 per annum. The manufacture even of 53 per cent. nitric acid in this manner yields a profit. The output [3] of the Zeche Lothringen in 1913 is stated to have been 150 tons of acid, but the yield is stated to have been less than 90 per cent.

The Ostwald process was the model on which the other platinum contact processes were based, and there was no fundamental difference between any of them. Whether the oxidation unit is placed vertically or horizontally is unimportant, and one of the first experimental plants of Ostwald and Brauer had a horizontal contact chamber. The yield depends mainly on the time of contact between

[1] See also *Chem. Ztg.*, 1915, "Repertorium," p. 65.
[2] *Chem. Ztg.*, 1914, p. 1015.
[3] Hesse-Grossmann, vol. iii., (1919), pp. 49, 50.

the catalyst and the gaseous mixture. As this factor has to be taken into account in all forms of construction, differences are confined to the choice of catalyst (platinum wire, foil, gauze, platinum asbestos, etc.), the manner in which it is fixed, its accessibility, and so forth.

K. Kaiser was the first to use platinum gauze, which he stretched across the bore of an iron tube. The wire which he used was 0·06 mm. in diameter (German Patent 271,517). The temperature required in order to start the reaction is not obtained by heating the catalyst, but by preheating the air to 300° to 400° C. The hot air is then mixed with ammonia, using a mixture containing 2 kg. of ammonia to about 50 cu. m. of air at a temperature of 350° to 370° C. The alleged advantages of Kaiser's process are that he can work with a considerable gas velocity ; in a tube of 200 mm. diameter and with a gas velocity of 120 cu. m. per hour, 8 kg. of ammonia can be oxidised per hour. It is stated that the dimensions of the tube are immaterial. According to the inventor, Kaiser's experimental plant at Spandau gave a yield of 95 to 97 per cent. during continuous working. According to German Patent 230,042, the air is activated by silent discharge or by heating in presence of platinum or palladium, by which means the yields are stated to be increased to more than 100 per cent., as under such conditions atmospheric nitrogen takes part in the reaction. It is stated that yields of 106 per cent. can be obtained with air containing ozone, as against 70 per cent. only without activation. Kochmann [1] was unable to confirm these results, which were later shown to be due to analytical errors. In the course of a controversy with the Berlin-Anhaltische Maschinenbau A.G. ("Bamag"), the firm which constructs the Frank-Caro oxidisers, Kaiser stated that by his process 370 kg. of ammonia could be treated per twenty-four hours with a gauze of 2,400 sq. cm. area, and that this quantity could be increased to 1,110 to 1,480 kg. of ammonia without allowing any unburnt ammonia to pass the contact unit.[2] An experimental plant was erected at Spandau in 1912 ; it was repeatedly inspected by German, French and American interested parties in the course of the years 1912 and 1913. Parsons [3] states that the Kaiser process, which was never applied on a manufacturing scale, is now obsolete.

According to Parsons' [4] report, to which we have already frequently referred, the Frank-Caro-Bamag group became interested in the catalytic oxidation of ammonia shortly after the commence-

[1] *Arb. a. d. Pharm. Inst. d. Univ.* (Berlin, 1911), vol. 8.
[2] *Chem. Ztg.*, 1916, pp. 14, 112.
[3] *J. Ind. Eng. Chem.*, **11**, 541 (1919).
[4] *Loc. cit.*

ment of the War. The only plant at work in Germany in August, 1914, was the small Gerthe plant of the Zeche-Lothringen. After Emil Fischer had emphasised the difficulty of covering the nitric acid requirements of Germany, the newly formed Munitions Department, under the leadership of W. Rathenau,[1] devoted attention to the matter, and energetically commenced to erect suitable works. The Bamag undertook the construction of oxidation units, according to the directions of A. Frank and N. Caro, and these were soon in successful use in various sulphuric acid works, where they replaced the Chile nitrate formerly used for the lead chambers. By the end of 1915 thirty plants, with a total monthly output of more than 100,000 tons of nitric acid, were partly under construction and partly finished. Several large works were provided with units of this type for the production of nitric acid from ammonia.

The constructional details became known in other countries through the premature publication of Schuphaus in *Metall and Erz.*[2] The platinum gauze was originally heated electrically, but this feature was abandoned in 1916, as it was found to be unnecessary during continuous manufacture. According to Kaiser,[3] the Frank-Caro-Bamag unit produced 30 kg. of ammonia daily per 400 × 600 mm. cross-section. The Bamag [3] has revised these figures to the effect that the first units oxidised 30 kg. of ammonia per twenty-four hours with 250 × 600 mm. area of gauze, and that by December, 1915, this output had been doubled. The units erected at that time had a capacity of more than 12,000,000 kg. of ammonia, and further units for a capacity of 17,000,000 kg. of ammonia were already under construction.

The utilisation of the Frank-Caro-Bamag units in conjunction with sulphuric-acid plants is described by H. Petersen.[4]

Fig. 62 represents a Frank-Caro-Bamag ammonia-oxidation plant as it was supplied, for example, for the oxidation of cyanamide ammonia. The ammonia, which is stored in gas holders at constant pressure, passes through the pressure regulator, *b*; an absolutely constant pressure of the ammonia is extremely important, and must be carefully supervised in every ammonia oxidation plant; it then passes into the mixing chamber, *d*. The air entering the oxidation system is filtered and passed by a fan through the tube, *f*, into the pressure regulator, *c*, from which it is supplied to the mixing chamber, *d*, in a regular stream. In *d* a uniform mixture of air and ammonia is obtained, as the ammonia is distributed over the whole cross-

[1] W. Rathenau, " Die Organisation der Rohstoffversorgung," 1915.
[2] 13, 21 (1916).
[3] *Chem. Ztg.*, 1916, p. 14.
[4] *Ibid.*, 1918, " Repertorium," p. 70.

section of the chamber, and thus mixed with the air. The mixture of air and ammonia leaves the mixing chamber below and passes into the distributing chamber, *g*, from which it passes to the lower end of the combustion units. These are provided with cast-iron cooling jackets. The actual catalyst chambers are interposed between *g* and the aluminium hoods, which are provided with sight-holes; the catalyst usually consists of platinum gauze, which may under circumstances be arranged in several layers. The average thickness of the platinum wire is 0·04 mm.; the gauzes contain

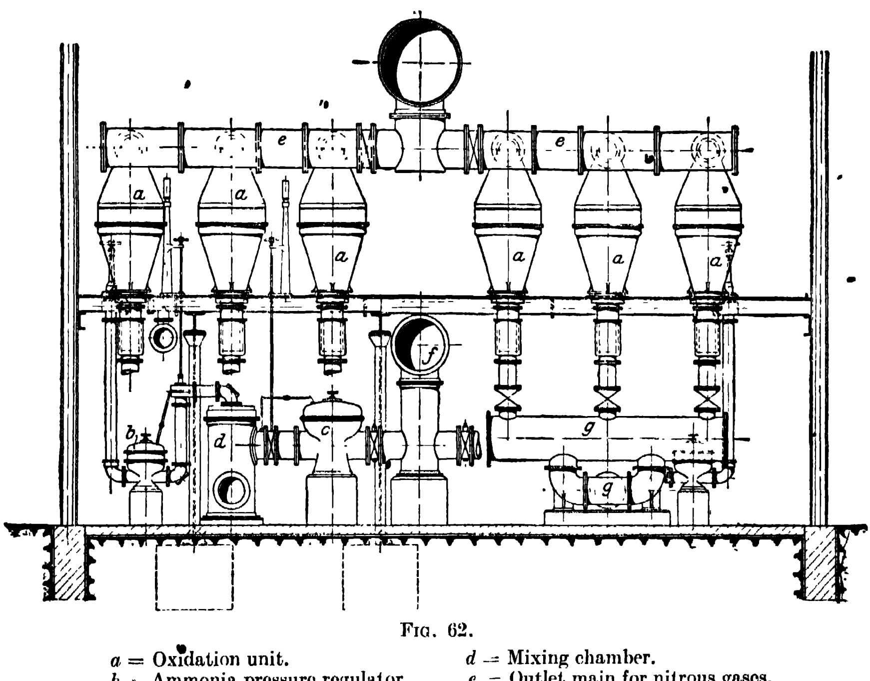

Fig. 62.

a = Oxidation unit. *d* = Mixing chamber.
b = Ammonia pressure regulator. *e* = Outlet main for nitrous gases.
c = Air pressure regulator. *f* = Air main.
g = Distribution pipe.

1,000 to 3,600 meshes per square centimetre. The output of the individual units necessarily depends on the working conditions, the purity of the gas and the magnitude of the unit. All gauzes require to be activated before they react properly with the gaseous mixture. It is advisable to wash them before use, first with benzine and then with acid free from halogen. After this they should be washed with alkali. It may be advisable at this point to emphasise the fact that free halogens act as extremely injurious catalyst poisons. The reaction gases from the contacts are carried to the nitric acid condensation plant through the common main, *e*. The gases in the dslivery mains below the contacts are maintained at a

slight excess pressure, which falls to atmospheric pressure at the catalyst gauze itself. In the upper portion of the hood the effects of the suction from the condensation plant become apparent.

German Patent 286,991 of the Bamag contains further information on such ammonia combustion plants. Neumann and Rose[1] give the following description of a platinum contact unit: platinum gauze of extremely fine mesh is held horizontally in silver-plated brass holders or an aluminium frame between two conical adapters of aluminium or of iron lined with aluminium. The gauze may be heated by a current of 120 to 150 amps. at 24 to 26 volts; it varies in area from 15 × 15 cm. to 1 × 2 m.

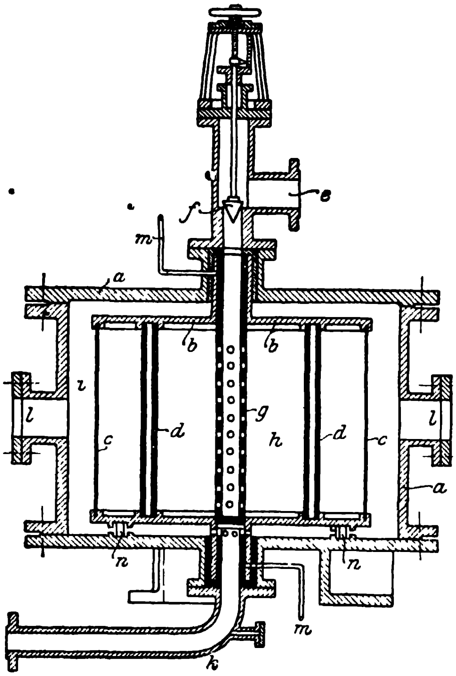

Fig. 63.

In German Patents 298,951 and 301,352 S. Barth describes another form of unit, the "Manfried" oxidiser (Fig. 63). The casing, *a*, contains a drum, *b*, the vertical circumference of which consists of a catalyst in the form of an insulated cylindrical platinum gauze, *c*. The arrangement is strengthened by struts, *d*, which hold the top and bottom plate apart; the bottom plate is in turn supported on projections, *n*, of the casing, *a*. The mixture of air and ammonia enters above through a delivery tube, *e*, and passes through the open valve, *f*, through a perforated porcelain tube, *g*, which forms the axis of the drum; from here it passes into the interior of the drum, *h*, and from there through the contact gauze, *c*, into the outer space, *i*. The reaction gases are removed through the tube, *k*, which ends in the centre of the base of the unit. The process can be watched by means of mica windows which close the openings, *l*, in the casing. An electric current for external heating can be passed through the terminals, *m*, should it be required. The contact gauze may also be placed horizontally, or may be

[1] *Zeitsch. f. angew. Chem.*, 1920, i., 55.

arranged to revolve. The Manfried oxidiser is stated to be intended mainly for use in connection with sulphuric acid chambers.

"Konstruktionsbureau Paul Hadamovsky-Berlin" recommends a catalyst of metallic cloth containing no platinum for the oxidation of ammonia.

On the basis of the Ostwald or Frank-Caro and Frank-Caro-Bamag processes, the catalytic oxidation of ammonia developed rapidly and independently in the United States. There were no ammonia combustion units in that country in 1914, but in 1919 the total output capacity of these plants was 225,000 tons of 100 per cent. nitric acid annually. So far, in both the United States and Germany, the oxidation of ammonia is the only synthetic nitric acid process which has become of real importance.

An electrically heated experimental platinum contact plant of the old type had been working since the spring of 1916 at the Niagara Falls Works of the American Cyanamide Company. As a result of the good results which were there obtained, the erection of the first large plant was commenced at the Ammo-Phos Works at Warners, N.J., in order to supply the necessary nitric acid for the 60,000 ton sulphuric acid works. The first six catalyst units started to operate in July, 1916. During actual working their output increased from 14 to 40 lb. of nitric acid per unit per hour. The platinum gauze had to be heated electrically, and had an area of about 2 sq. ft. The ammonia was supplied directly from the cyanamide decomposers, which together produced about 30 tons of ammonia gas daily.

For the erection of Government plant an affiliated company of the American Cyanamide Company was formed, namely, the Air Nitrate Corporation, which erected an ammonia oxidation plant at Sheffield (Ala.) of an annual output capacity of 90,000 tons of nitric acid.[1] The works comprised six catalyst sheds, which covered an area of 50 × 210 feet, and each contained four rows of 29 units each —that is, 696 in all. Each unit contained 143 grm. of platinum.

Meanwhile the work of the Semet-Solvay Company, which had studied the oxidation of ammonia at its experimental plant at Syracuse, in conjunction with the Bureau of Mines, since August 10th, 1916, led to notable results. Although other metallic and non-metallic contact materials had given satisfactory results, the use of platinum was retained. A new element resulted of the so-called Jones-Parsons type.[2] Electric heating, which was initially used, was finally relinquished altogether, after the number of platinum

[1] E. J. Pranke, *Chem. and Met. Eng.*, **19**, 396 (1918).
[2] Parsons, *J. Ind. Eng. Chem.*, **11**, 541 (1919).

gauze spirals had been increased to three. An experimental plant was also sent to Brunner, Mond & Co., Ltd., in England.

The principle of the new unit is shown in Fig. 64. The gases enter above and pass through the platinum gauze contact, which consists of wire of about 0·066 mm. thickness and contains 80 meshes per inch. The gauze weighs about 500 gm. In this case, also, if a good yield of nitric oxide is to be obtained, it is necessary that the gases should be free from iron oxide, oil, phosphorus compounds, organic constituents, and so forth. With perfectly pure gases, the unit produces about 2·25 tons of 100 per cent. nitric acid daily, at a gas velocity of 6·66 cu. m. per minute, and with a yield of 90·7 per cent., or of 2·75 tons with a yield of 87 to 88 per cent. Aluminium mains are used to carry the gases to the plant. For the exit gases iron tubes can safely be used as long as the gases have a temperature above 175° to 200° C. The contact units themselves are constructed of cast iron, or of boiler plate, and are lined with fireproof tiles. In 1918–19 this unit cost about $200, apart from the platinum. The platinum gauze consists of a strip 13 inches wide and 113·5 inches long, which is rolled into the form of a cylinder 9 inches in diameter containing four layers. The cylinder of 80-mesh gauze and 260·00 mm. wire weighs 16·5 oz. The gauze is conveniently activated by electric heating; after the reaction has once been started by heating a portion of the gauze with a small flame, no further external heating is required if the gases are pure. External heating is only required with impure gases or if they contain less than 10 per cent. of ammonia. In preheating the gases care is taken that no substances other than nickel, aluminium or quartz come into contact with the hot gases. All other materials have a rapid decomposing action.

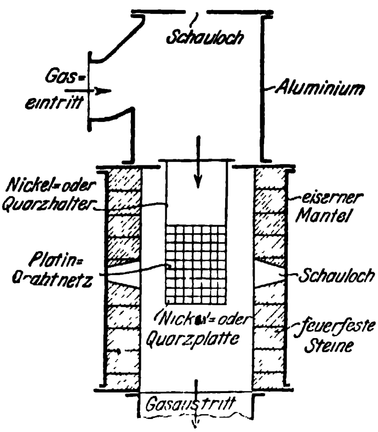

FIG. 64.

Schauloch = Inspection hole.
Gaseintritt — Gas inlet.
Nickel-oder Quarzhalter = Nickel or quartz support.
Eiserner Mantel = Iron casing.
Platin-drahtnetz = Platinum gauze.
Nickel-oder Quarzplatte = Nickel or quartz plate.
Feuerfeste Steine = Fire-proof bricks.
Gasaustritt — Gas exit.

Careful observations were made of a working Jones-Parsons unit at the Syracuse plant, for example, from April 25th to May 18th, 1918. With mixtures containing 8·22 to 11·85 volumes per cent. of

ammonia and at velocities of 150 to 250 cu. ft. per minute, 83 to 98 per cent. yields of nitric oxide were obtained. The average value was a 90·7 per cent. yield with 10·57 per cent. of ammonia by volume. Another unit was operating continuously from February 23rd to September 15th, 1918, without the necessity for any repairs. Interruption then occurred through the entry of alkaline liquor into the unit, and an average yield of 91·4 per cent. was obtained. The most favourable result which was recorded was as follows : 10·5 per cent. by volume of ammonia ; gas velocity, 200 cu. ft. per minute ; temperature, about 825° C. ; yield, 94 per cent. ; output, 208 lb. of nitric acid per hour, that is, 21·7 lb. per square foot of catalyst surface, or 14·1 lb. per ounce of platinum.

Parsons' data of results obtained on the Muscle Shoals plant are extremely interesting. If electric heating were employed on that plant the electric requirements would be 5·5 h.p. In 1917 to 1918 the cost of a plant for the production of 25,000 tons of 100 per cent. nitric acid annually was as follows :—

	Per ton per year.
In the form of 50 per cent. acid	$45
In the form of 94 per cent. acid	$60

The manufacturing costs were as follows :—

	Per ton of 100 per cent. HNO_3.
Manufacture in the form of NO gas	$ 5 + cost of ammonia.
Manufacture in the form of 50 per cent. HNO_3	$15 + ,, ,,
Manufacture in the form of 94 per cent. HNO_3	$30 + ,, ,,

For comparison, the manufacture of 1 ton of 100 per cent. HNO_3 in the form of 94 per cent. acid from Chile nitrate cost $48, apart from the cost of the nitrate.

W. S. Landis [1] states that the first continuous experiments of the American Cyanamide Company with cyanamide ammonia resulted in a 92·4 per cent. yield, and that in individual experiments at the Warners plant, New Jersey, a maximum yield of 96 per cent. was obtained.

The nitric acid plant at Muscle Shoals [2] comprises sheds for the oxidation units, oxidising towers, coolers and absorption plant. The six catalyst sheds have an area of 15·3 × 64 m., and are each divided into two separate portions. The western portion contains the gas meters, and is traversed by air mains of 1·5 m. diameter, which are carried underground and supplied by centrifugal fans. The ammonia gas from the autoclaves is received in two gasholders holding 535 cu. m. The gas is accurately measured, and then mixed

[1] *Chem. Eng.*, 27, 113 (1919).
[2] *Met. Eng.*, 20, 8 (1919).

with air in the proportion of 1 to 9 or 10. The mixture traverses twelve iron mixing chambers of 2·44 m. diameter and 9·15 m. height, which are filled with spiral ring packing. It passes from these mixing chambers into the oxidation units.

Each of the 6 sheds contains 4 rows of 29 units each; thus the whole plant contains 696 units. The units are separated by intervals of 1·53 m., and each two units have a common switch-board controlling the supply of current. The mixed gases pass from above through an iron tube into the rectangular aluminium container, of about 355 × 710 mm. cross-section and 1,520 mm. high, in the base of which the catalyst gauze is fixed. The platinum gauze is woven of wire of 0·0066 mm. diameter and contains 80 meshes per inch. Each layer weighs about 143 gm. Each unit comprises an 8 kw. transformer which transforms current of 460 volts down to 21 volts, and during normal working requires 365 amps. when heating is necessary at all. The temperature of the gauze is thus raised to 730° C. The combustion process can be observed through sight holes and controlled. The reaction gases leave the unit below through a cast-iron tube which enters a gas main lined with tiles and acid-proof cement, by which they are carried into the oxidising towers and coolers.

The tower shed has an area of 30·5 × 183 m., and contains 24 high-temperature coolers, which consist of horizontal water tube boilers, which generate steam at 2 atm. pressure; in these the gas is cooled from 600° to 200° C. These boilers are connected by aluminium mains with 12 low-temperature water coolers. These latter are rectangular chambers which are divided by partitions into 5 divisions. The gas is compelled to traverse these divisions in a zigzag path. From the roof of these chambers there are suspended 140 tubes closed below, 2·5 m. long and 127 mm. in diameter, into which cooling water is passed from a central delivery tube. In these cooling chambers the temperature of the gases is lowered to such a point that liquid nitric acid commences to separate; this is, however, heavily contaminated with nitrogen oxides, and is therefore collected in special separators. In the first two chambers the cooling tubes are constructed of stoneware, but in the others are of duriron, which is iron containing 15 per cent. of silicon.

The gas leaving the low temperature coolers, containing a mixture of nitric oxide and nitrogen dioxide, then passes into the oxidising towers, where further dioxide is formed. These towers, which have a base area of 1·45 sq. m., are collected in groups of four. They are built of acid-proof masonry, and are traversed by the gases

alternately upward and downward. The gases leaving these oxidising towers contain practically all their fixed nitrogen in the form of tetroxide. They then pass into the absorption towers.

The shed containing the absorption towers lies to the south-west of those just described; it covers an area of 80·5 × 183 m. and contains 6 sets of 12 towers each. These are constructed of acid-proof masonry and cement in a strong iron casing, which is protected from corrosion by acid by a thick layer of pitch. They are of square cross-section, 10·7 m. in diameter, and are 18·3 m. high. Each is divided into four vertical shafts, similarly to the oxidation towers. The first of these is half filled with spiral rings, 152 mm. in diameter, and above with large rings, 56 mm. in diameter. The second division is completely filled with the smaller size of filling. Dilute acid trickles down these towers in such a manner that each division receives the liquid from the base of the preceding division. The liquid is raised by compressed air from aluminium pressure pots, of which 96 are working and 24 in reserve. The shed contains 120 wells, each 300 mm. in diameter, and 30·5 m. deep. The aluminium pressure pots and pressure tubes are suspended in these wells on duriron girders; they are operated by compressed air at about 8 atm. pressure, and are cooled externally by the water. A system of electrical resistance meters in the cooling water of each well, provided with signal lamps, automatically indicates any leakage of acid into the water.

The last tower supplies an acid of 50 per cent. concentration, and the top of each division of each tower contains an air separator and an acid distributor. Between the first and second towers of each division an aluminium fan is installed which serves to circulate the gases. At the end of the second tower the effluent gases are discharged into the air. The conduits for the acid discharged at the bases of the towers consist of 100 mm. duriron tubes, and lead to the aluminium pressure pots.

The dilute acid is collected in 12 aluminium weighing vessels, 3 m. in diameter and 3·65 m. high, from which it passes to 12 storage vats, 7·5 m. in diameter and 3 to 3·5 m. high. From these the acid passes to the ammonium nitrate plant, of which the neutralising shed covers an area of 28·4 × 45·4 m. and contains 4 absorption towers, 2 mixing tanks, 4 condensers, 4 neutralising tanks, 4 settling tanks, 1 storage tank, and 3 filter presses. Eight settling tanks stand in the open. The nitric acid passes from the storage tanks into a mixing vessel, from which it is raised by means of a pressure pump into one of the absorption towers, which are of square cross-section, 213 mm. in diameter and 6·10 m. high, and are

filled with 75 mm. rings. The ammonia which escapes fixation in the neutralising tanks rises in the towers, in which it is absorbed. The acid liquid from the towers passes into a second mixing vat, then into the distributor of a second tower, and from there into the neutralising tank. In this the acid liquid is continually maintained at a level of 90 cm., and ammonia gas is passed into this liquid from above through a delivery pipe about 43 cm. wide. The effluent gases pass through a condenser similar to the low temperature coolers already described, but smaller, and are then freed from any remaining ammonia in the absorption towers. The completely neutralised liquid from the neutralising tank is collected in a storage tank. It traverses 8 settling and clarifying basins before it is evaporated.

This liquid is evaporated and crystallised in 5 special buildings, each covering 18·3 × 36·6 m.; in order to avoid fire and explosion risks these are 500 m. apart, and at a similar distance from any other structure, and are situated at the southern end of the works. Ammonium nitrate liquor and steam are supplied by mains 152 mm. in diameter. Compressed air and ammonia are supplied by a system of 63-mm. mains. During evaporation ammonia has to be continuously added, as the liquid readily becomes acid. Each building contains a liquor reservoir of 3 m. diameter and 3·65 m. high and 10 evaporating pans. These are lined internally with blue enamel, and are about 3·35 m. long, 1·9 wide and 0·85 m. deep. Six steam coils of 76 mm. aluminium tube pass up and down each of these pans. There are also three 13-mm. air pipes, which accelerate evaporation and render it more regular by a current of air. A spray catcher is suspended over each pan. The evaporating pans are so arranged on five supports at a height of 45 cm. above floor level that the air outside the shed has free access, and the process can readily be controlled at any time. Each evaporator is furnished with two open cooling boxes with steam and cold water coils, and with a stirrer making 17 revolutions per minute. The solution leaves the evaporating pans at a temperature of 145° C. It is then slowly cooled in a cooling pan, first by steam and then by water, with continuous stirring. The coarse crystalline paste is discharged below and dried on the floor of the building.

The nitric acid and ammonium nitrate plants at Muscle Shoals are intended for a production of about 300 long tons of ammonium nitrate per twenty-four hours (about 110,000 metric tons per annum).

According to C. Bosch [1] lengthy researches were necessary by

[1] *Chem. Ztg.*, 1920, pp. 721–722, and *Zeitsch. f. Elektrochem.*, 1918, p. 361; *Year-book of the Halle Association for the Investigation of the Mineral Wealth of Central Germany*, 1919, No. 1, p. 130.

the B.A.S.F. in order to obtain an iron-oxide catalyst suitable for the oxidation of ammonia on the manufacturing scale. It is well known from the patent literature that not only the B.A.S.F., but also the other large firms of the I.G., have attacked this problem with great activity. All that is necessary here is to give a short sketch of the method actually employed on the manufacturing scale.[1] According to Neumann and Rose,[2] the iron-oxide mixture, which may contain bismuth, is used in layers 10 to 12 cm. thick on perforated plates in reaction towers, 5·5 m. high and 4 m. in diameter. The preheated gaseous mixture enters tangentially above and leaves the tower below. The temperature is maintained at 700° to 800° C. The yield is 80 to 85 per cent.

The Farbenfabriken vorm. Fr. Bayer & Co., at Leverkusen,[3] mix the ammonia obtained from concentrated ammonia solution with preheated air and pass it into the oxidising chambers at a temperature of 250° C. The catalyst units are still more or less in an experimental stage, although the principles of their construction are well established. Those used at Leverkusen are of 4·25 m. diameter and 5·50 m. high. The contact material consists of granular iron oxide, which is mixed with the oxide of another heavy metal (bismuth) and passed through a 6-mesh (per centimetre) sieve. The contact mass is supported on perforated stoneware grids in layers 10 to 12·5 cm. thick. The gases to be oxidised, containing 7 to 10 per cent. by volume of NH_3, are passed tangentially into the upper part of the furnace, the temperature of which is 700° to 800° C. They traverse the catalyst from above downward and leave the furnace below, a yield of 80 to 85 per cent. of nitric oxide being obtained. The reaction gases first pass through a condenser, and then through several series, each of six absorption chambers, which are charged with saturated sodium carbonate solution. The first tower is constructed of granite and the remainder of wrought iron. They are 40 feet high and 5 feet in diameter. Solutions are finally obtained containing 350 gm. of $NaNO_3$ per litre, which are concentrated in vats with stirrers and allowed to crystallise. At the commencement of 1919 the output capacity of the Leverkusen plant was 6,000 to 7,000 tons of nitrate monthly. During the War the reaction gases from the furnaces were converted directly into nitric acid. The monthly output reached 1,000 to 1,500 tons of 77 to 78 per cent. acid (1·45 to 1·455 sp. gr., or about 45° Bé.). The gases were passed through 12 granite towers

[1] *Zeitsch. f. angew. Chem.*, 1916, p. 208.
[2] *Loc. cit.*, 1920, i., p. 55.
[3] *Chem. Ztg.*, 1919, p. 809 ; 1920, p. 838.

18 m. high and 5·5 m. in external diameter, which were arranged in two parallel series of six each. The first ten towers were supplied with water or dilute acid and the last two with sodium carbonate solution. The third or fourth pair of towers yielded the strongest acid, containing 40 to 47 per cent. of HNO_3 (29° to 33° Bé.). The towers were not utilised to their full capacity, as they were too large. The tower acid was concentrated with the help of sulphuric acid by steam and by a portion of the hot combustion gases from the furnaces. The dilute sulphuric acid was passed through a Kessler plant of 20 small units. At that time the whole arrangement did not work very satisfactorily. The concentration plant often required serious repairs and was very expensive to work. It is stated that centrifugal pumps and tubes of ferro-silicon did not give satisfaction on this plant.

A large number of workers have endeavoured to determine the exact part played by the catalyst in the combustion of ammonia and the manner in which it operates. The view of Wenger and Urfer [1] is interesting; they consider that the presence of the catalyst primarily causes the ammonia molecule to decompose in such a manner that loose compounds of hydrogen and the catalyst metal are formed. The nitrogen is then oxidised whilst in the nascent state by oxygen. According to K. Glaser,[2] ammonia is decomposed by nickel with formation of its constituent elements at 630° C. On the other hand, C. Waldeck [3] (German Patent 281,096) finds that nickel causes decomposition at 500° to 550° C. See also articles by C. Paal and W. Hartmann,[4] E. B. Maxted,[5] K. W. Rosenmund,[6] M. Busch,[7] German Patent 312,726 and U.S. Patent 1,345,323.

The electro-chemical oxidation of dissolved ammonia has also often been proposed. E. Müller and Spitzer [8] carried out much work on this subject, and were able to oxidise ammonium carbonate smoothly to ammonium nitrate at platinum anodes with a yield of 96·7 per cent. Brochet and Boiteau [9] obtained 0·297 gm. of HNO_3 and 0·377 gm. of $NH_4.NO_3$ per ampere hour. Cohn and Geisenberger proposed to employ electrolytic oxidation, using water saturated with air (Swedish Patent 19,895). The Elektrochemischen Werke G.m.b.H. oxidise a solution of NO_2 in nitric acid and obtain the pure acid (German Patent 231,546); according to German

[1] *Zeitsch. f. angew. Chem.*, 1918, ii., 395.
[2] *Loc. cit.*, 1918, ii., 248.
[3] *Chem. Ztg.*, 1915, "Repertorium," p. 14.
[4] *Ber.*, **51**, 711 (1918).
[5] *Chem. Zentralbl.*, 1920, iv., 358.
[6] *Chem. Ztg.*, 1920, p. 733.
[7] *Ibid.*, p. 751.
[8] *Zeitsch. f. Elektrochem.*, **11**, 917 (1905); see also *Chem. Ztg.*, 1913, No. 110.
[9] *Chem. Ztg.*, 1909, p. 629.

Patent 233,895, on the other hand, it is possible by electro-reduction of HNO_3 at aluminium cathodes smoothly to obtain ammonium nitrate.[1] According to German Patent 85,103 of Siemens and Halske, ammonia is oxidised by the dark electric discharge.

The Swiss work already cited opens up the possibility of a technical application of the catalytic reduction of nitrogen oxide with formation of ammonia. In the *Helvetia Chimica Acta* of the Swiss Chemical Society, Guye and Schneider describe in detail the decisive experiments [2] which they carried out with nickel at 250° to 300° C. B. B. Adkikary also discusses these questions.[3] The observations of C. Rossi on this question are also of interest (French Patent 463,821); he finds that the oxides of iron, manganese, tin and copper decompose nitric oxide catalytically, whilst alumina and silica have no such action. See also, with regard to the catalytic oxidation of ammonia, British Patent 3194/1913 and French Patent 465,045.

Supplement, 1921-24

Articles of general interest will be found in *Trans. Amer. Elec. Soc.*, **35**, 283 (1920); *Chem. and Met. Eng.*, **22**, 125 (1920); **26**, 1217 (1922); *Chem. Age*, **4**, 150 (1921); **7**, 115, 200 (1922); *Journ. Soc. Chem. Ind.*, **40**, 185 (1921); **41**, 37 (1922); *Giorn. Chim. Ind. Appl.*, **3**, 408 (1921).

Patent activities are mainly concerned with the choice of suitable catalysts ($CuO + Pb(NO_3)_2$; platinum, sodium chromi-silicate, bauxite, $CO_2O_3 + Al_2O_3$; rhodium-asbestos, vanadium oxide, Al_2O_3; silica gel, active carbon), or with the construction of the elements. The patents in question are:—

B.A.S.F. and co-patentees: German Patents 301,362, 303,241, 303,331, 307,001, 334,975; U.S. Patent 1,379,387; Austrian Patent 88,279.

Frank and Caro: German Patents 303,822, 303,823, 303,824, 304,269.

Barth: German Patents 298,951, 301,352.

Frischer: German Patent 301,681; Austrian Patent 87,289; British Patent 146,227/1920.

Permutit A.G.: German Patent 298,981.

Lecesne: German Patent 322,843.

Scott; General Chemical Company; Atmospheric Nitrogen Corporation: British Patent 136,158/1919; U.S. Patent 1,399,807; Norwegian Patent 33,125; also U.S. Patents 1,420,201, 1,391,332;

[1] See also German Patent 175,480 of G. E. Cassel; *Electr. and Met. Ind.*, 1907, v., 449.
[2] *Chem. Ztg.*, 1918, pp. 273, 432.
[3] *Chem. News*, **112**, 163 (1915).

Norwegian Patent 35,048 ; British Patent 133,041/1919 ; German Patent 342,094 (*Metallbörse*, **1923**, 1979 ; *Jour. Am. Chem. Soc.*, **43**, 2034 (1921) ; *Chem. Ztg.*, **1922**, 343, 910).

The investigations of Decarrière on catalyst poisons, and cyanamide ammonia are extremely instructive (*Bull. Soc. Chim. de France* (4), **25**, 489 ; *Compt. rend.*, **172**, 1663 ; **174**, 460, 256 ; see also French Patent 498,114 and British Patent 181,486/1921).

Other oxidation reactions of ammonia are dealt with in the *Gazz. Chim. ital.*, **51**, 225 (1921) ; U.S. Patent 1,400,912 ; Swiss Patent 87,562.

CHAPTER XXVI

The Conversion of Nitrogen Oxides into Nitric Acid

FROM the above pages it will be clear that the conversion of nitrogen oxides from the arc process or ammonia oxidation process into nitric acid is preceded by the oxidation of nitric oxide to nitrogen dioxide.

In their work on the theory of the lead-chamber process, both Lunge and Berl [1] and Raschig [2] studied the velocity of this reaction. In their investigations Lunge and Berl assume a perfectly normal reaction, according to the tri-molecular equation :—

$$2NO + O_2 = 2NO_2,$$

an equation of the third order, whilst Raschig detects an inflection point of the reaction curve, after a 50 per cent. conversion, corresponding to the production of nitrogen trioxide, which is then in turn oxidised to the dioxide at a slower rate.

These contradictory results were followed by a series of investigations by M. Bodenstein, with the object of definitely settling the question. A preliminary report before the Congress of Applied Chemistry in London in 1909 [3] was later completed by a lecture before the Deutsche Bunsengesellschaft in April, 1918.[4] In order to be able to follow the reaction quantitatively, the pressure was reduced to about 1/30 atm. ; at this pressure time intervals as long as one hour may be required for a 90 per cent. oxidation. In the ingenious laboratory apparatus the decrease of pressure was controlled by a manometer containing bromonaphthalene. The reaction takes place strictly according to the equation for a reaction of the third order—

$$\frac{d_x}{d_t} = k.[NO]^2.[O_2],$$

that is, according to the equation of Lunge and Berl. The constants in molecules per cubic centimetre and minutes are—

At 0°C. $2{\cdot}10 \times 10^6$,
,, 30° ,, $1{\cdot}69 \times 10^6$,
,, 60° ,, $1{\cdot}34 \times 10^6$,
,, 90° ,, $1{\cdot}08 \times 10^6$,

[1] *Zeitsch. f. angew. Chem.*, **19**, 861, 1717.
[2] *Loc. cit.*, **18**, 1281 ; see also *loc. cit.*, **17**, 1398, 1777 (1904) ; **18**, 67 (1905) ; **19**, 807, 857, 881 (1906) ; **20**, 694, 1713 (1907).
[3] *Zeitsch. f. angew. Chem.*, **22**, 1153 (1909).
[4] *Loc. cit.*, 1918, i., 145 ; iii., 247 ; *Chem. Ztg.*, 1918, p. 202.

that is, they decrease with increasing temperature; they are not influenced by the addition of water-vapour, sulphur dioxide or nitrogen dioxide.

Two molecules of NO_2 partially unite to form 1 molecule of N_2O_4. The velocity at which this equilibrium is attained is extraordinarily rapid. It progresses very far at intervals of the order of 1/2000 of a second, as was shown by Keutel's [1] determinations of the velocity of sound in nitrogen dioxide. The equilibrium constants have been determined by Natanson and by Schreber.[2]

Raschig's figures, which are not in agreement, are easily explained by the properties of the mixture of nitric oxide and nitrogen dioxide, which always behaves as the trioxide, N_2O_3, when both ingredients are present in equal proportions, although vapour density determinations show that appreciable quantities of this substance cannot be present. Le Blanc [3] and Foerster [4] have elucidated these conditions in great detail. Nitric oxide and dioxide are always in equilibrium with the trioxide, an equilibrium which is attained with extreme rapidity :—

$$NO + NO_2 \rightleftharpoons N_2O_3.$$

In distinction to its two components, nitrous anhydride, N_2O_3, has the property of dissolving with extreme rapidity in caustic alkali solution or in sulphuric acid :—

$$N_2O_3 + 2NaOH = 2NaNO_2 + H_2O,$$
$$N_2O_3 + 2H_2SO_4 = 2HSNO_5 + H_2O.$$

The nature of his experimental arrangements therefore necessarily led Raschig, as we now know, to an erroneous result. Nitrogen dioxide reacts with alkalis much more slowly, according to the equation :—

$$2NO_2 + 2KOH = KNO_2 + KNO_3 + H_2O.$$

Nitric oxide [5] boils at $-153{\cdot}6°$ C., melts at $-167°$ C., has a critical temperature of $-93{\cdot}5°$ C. and a critical pressure of 71·2 atm. It is oxidised by oxygen much more rapidly at 0° than at 100° C., presumably because at low temperatures a super-oxide, $NO.O_2$, is formed which favours the reaction

Nitrogen trioxide or sesquioxide has a melting point of $-111°$ C.; at sufficiently low temperatures it forms an indigo blue liquid, which commences to decompose at $-10°$ C. At $-2°$ C. nitric

[1] F. Keutel, "Über die spezifische Wärme von Gasen," "Dissertation" (Berlin, 1910).
[2] *Zeitsch. f. physic. Chem.*, **24**, 651 (1897).
[3] *Zeitsch. f. Elektrochem.*, **12**, 541 (1906).
[4] *Zeitsch. f. angew. Chem.*, **23**, 2017 (1910).
[5] K. A. Hofmann, "Lehrbuch der anorganischen Chem.," 2nd edition (Brunswick, 1919).

oxide is evolved, and is followed later by the dioxide. The hydrate of the trioxide is nitrous acid, which is only known in aqueous solution. Even the solution decomposes at the ordinary temperature, according to the equation :—

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

Nitrogen dioxide or peroxide, NO_2, of melting point $-9°$ and boiling point $+22°$–$23°$ C., is only stable below $+150°$ C.; the following reaction then commences—

$$NO_2 = NO + O,$$

and is complete at 620° C. Between $+100°$ C. and $+150°$ C. the gas is of an intensive brown colour, which becomes lighter as the vapour is cooled, and at $+22°$ C., at atmospheric pressure, a reddish-brown liquid is finally obtained which is yellowish-red at $+15°$ C., yellow at $+10°$ C., and forms colourless crystals at $-9°$ C. The vapour density rapidly rises with decreasing temperature and indicates the formation of double molecules, N_2O_4, nitrogen tetroxide. Below 0° C. both the crystals and the liquid contain substantially this colourless polymer. At $+64°$ C. the equilibrium—

$$N_2O_4 \rightleftarrows 2NO_2$$

is so far displaced that half the substance is present as colourless N_2O_4, and the other half as reddish-brown dioxide, NO_2. At $+150°$ C. and 1 atm. pressure it is practically all converted into molecules of the dioxide. The dissociation into molecules of nitrogen dioxide entails an increase of volume, and is therefore favoured by decrease of pressure. The crystallised tetroxide reacts with water at $-20°$ C. with formation of nitric acid and the trioxide or nitrous acid. Under certain conditions two layers are formed, an upper one of nitric acid, slightly green in colour, and a lower, deep blue layer of the trioxide.

Nitrogen pentoxide, N_2O_5, has a melting point of 29·5° C. and boils at 45° C. with initial decomposition. It is formed by oxidising the tetroxide with ozone. Below $+8°$ C. the crystals of the pentoxide are of a pure white colour. It reacts with water with evolution of heat (16 cals. per molecule of N_2O_5) and formation of nitric acid.

Nitrous oxide, N_2O, boils at $-89·4°$ C., and melts at $-102·3°$ C.; its critical temperature is $+38·8°$ C., and its critical pressure 77·5 atm. It is also known as "laughing gas"; it is formed by the decomposition of molten ammonium nitrate, when heated to 170° C. :—

$$NH_4NO_3 = N_2O + 2H_2O + 30 \text{ cals.}$$

The behaviour of the individual oxides of nitrogen fully explains the phenomena which occur during their technical absorption to form

nitric acid. The hot reaction gases, containing nitric oxide, must be strongly cooled, so that they may react as far as possible with excess of air to form the dioxide. The mixture of monoxide and dioxide reacts in contact with absorbing agents such as water, with formation of nitrous acid. This latter is unstable and decomposes with formation of nitric acid and nitric oxide. The latter then takes part in the reaction already described ; these reactions may be summarised by the comprehensive formula :—

$$4NO + 3O_2 + 2H_2O = 4HNO_3.$$

Nitrogen dioxide, on the other hand, forms the tetroxide, which then reacts as follows :—

$$N_2O_4 + H_2O = HNO_3 + HNO_2.$$

The predominance of the one reaction or the other will be discussed later.

When commercial nitric acid of 98 to 99 per cent. purity is cooled to $-41{\cdot}3^\circ$ C., snow-white crystals of pure nitric acid, HNO_3, of boiling point $+86^\circ$ C. at 760 mm. pressure, and melting point $-41{\cdot}3^\circ$ C., are formed ; these become yellowish, even below 0° C., as nitrogen oxides are formed. At ordinary pressures the pure acid boils with partial decomposition, yielding a distillate which contains only about 98 per cent. of nitric acid. At 24 mm. pressure pure nitric boils at $21{\cdot}5^\circ$ C. The specific gravity of an acid of 99·7 per cent. HNO_3 is 1·5204, and of an acid of 52·35 per cent. HNO_3 1·3299. Lunge and Rey have published accurate tables of specific gravities of nitric acid of various strengths. More dilute acids always boil at a higher temperature than pure HNO_3. When a 20 per cent. solution is distilled water passes over first until at $120{\cdot}5^\circ$ C. the so-called minimum mixture follows, containing 68 per cent. of HNO_3 ; its specific gravity is 1·41, and it does not fume. Further concentration by simple distillation is impossible.

By the action of light, and on distillation, partial decomposition occurs, according to the equation :—

$$4HNO_3 \rightleftarrows 4NO_2 + 2H_2O + O_2.$$

The constitution of the anhydrous acid corresponds to the formula :—

O

OH

Such an acid contains no hydrogen ion, which is only present when it is considerably diluted, and in solutions of its salts. At ordinary concentrations equilibrium occurs between the two forms. Definite

hydrates, such as $NO(OH)_3$ or $N(OH)_5$, do not exist, according to Hofmann.

In a lecture before the Académie des Sciences in Paris on February 10th, 1919, A. Sanfourche [1] showed that the oxidation of nitric oxide to the trioxide by dry air is complete at all temperatures between $-50°$ C. and $+600°$ C. within a fraction of a second. The further oxidation to tetroxide depends on the equilibrium—

$$2N_2O_3 + O_2 \rightleftarrows 2N_2O_4,$$

which tends to an increased reversion to the trioxide as the temperature increases. The equilibrium proportion of tetroxide at various temperatures is as follows :—

	Per cent.
At 100° C.	100·0
„ 200° „	89·9
„ 280° „	83·7
„ 340° „	52·3
„ 400° „	28·7
„ 450° „	13·4
„ 525° „	0·8

The views of Sanfourche are directly opposed to those experiments of German investigators which we have already described. There is an article on the electrolytic protential of the conversion of nitrite into nitrate + nitric oxide in the *Zeitsch. f. Elektrochem.*, **26**, 182 (1920). P. Ch. Rây, M. L. Dey and J. Ch. Ghosh [2] determined the velocity constant of the decomposition of nitrous acid, which was found to be a monomolecular reaction, and found 0·00014 at 0° C., 0·00022 at 21° C. and 0·00057 at 40° C. The maximum concentration of nitrous acid at 0° C. is 0·185 N., and its dissociation constant is 6×10^{-4}.

In the *Zeitsch. f. angew. Chem.*[3] F. Foerster, Th. Burchardt and E. Fricke published a detailed account of their work on the production of concentrated nitric acid from nitrous gases. The primary reaction—

$$N_2O_4 + H_2O \leftrightarrows HNO_3 + HNO_2$$

results in an equilibrium when the nitric acid has attained a certain concentration of about 50 per cent. HNO_3. Equilibrium with nitrous acid results, according to the equations—

$$3HNO_2 \rightleftarrows HNO_3 + 2NO + H_2O$$

and

$$2HNO_2 \rightleftarrows N_2O_3 + H_2O.$$

[1] *Chem. Ztg.*, 1919, p. 232 ; *Chem. Zentralbl.*, 1919, iv., 360.
[2] *J. Chem. Soc.*, **111**, 413 (1917) ; *Zeitsch. f. angew. Chem.*, 1918, ii., 196.
[3] (1920) i., 113, 122, 129.

Moreover, the following equilibria result in the gaseous phase :—

$$N_2O_4 \rightleftarrows 2NO_2$$

and

$$NO_2 + NO \rightleftarrows N_2O_3.$$

If, therefore, the nitric acid is to be further concentrated it is necessary to remove the nitrous acid which is formed. This is achieved most simply by passing a current of nitric oxide and oxygen or air through the liquid.

The combination of oxygen and nitric oxide, when these are passed through water or dilute nitric acid, is very rapid [1] as long as the concentration of the acid is low. Above a concentration of about 55 per cent. HNO_3, and at the ordinary temperature, the absorption and formation of nitric acid gradually becomes slower, and above 65 per cent. of HNO_3 there is a still more considerable decrease in the reaction velocity. Nitric acid containing 64·2 per cent. of HNO_3 barely absorbs 10 per cent. of the dioxide, when a mixture of 10 litres of nitric oxide and 24 litres of oxygen is bubbled through it during a period of four hours, with formation of a 68·4 per cent. nitric acid.[1] Klaudy [2] ascribes the retardation of the reaction to the formation of hydrates, and in fact Küster and Kremann [3] find that the substances $HNO_3 . H_2O$, containing 77 per cent. HNO_3, and $HNO_3.3H_2O$ containing 54 per cent. HNO_3, may be obtained on freezing aqueous nitric acid. Foerster and his associates assume that these hydrates also exist in aqueous solution, and that the various concentrations of acid may be expressed by the following equilibria :—

Above 54 per cent HNO_3; $HNO_3, 3H_2O \rightleftarrows HNO_3, H_2O + 2H_2O$.

Above 77 per cent. HNO_3; $3HNO_3, H_2O \rightleftarrows HNO_3, 3H_2O + 2HNO_3$.

Ssaposchnikow [4] gives the further equilibrium—

$$2HNO_3 \rightleftarrows N_2O_5 + H_2O$$

as probably occurring in acids containing more than 88 per cent. HNO_3. The circumstance that the conversion of nitric oxides, oxygen and water into nitric acid is greatly retarded if more than 55 per cent. of HNO_3 is present—that is, on exceeding the stage of hydration, $HNO_3.3H_2O$—is in agreement with these views.

As a result of earlier experiments, Foerster and Koch [5] came to the conclusion that the limiting concentration of nitric acid which can be attained by the action of nitric oxide and excess of oxygen

[1] *Zeitsch. f. angew. Chem.*, **21**, 2161, 2209 (1908).
[2] *Zeitsch. f. Elektrochem.*, **12**, 547 (1906).
[3] *Zeitsch. f. anorg. Chem.*, **41**, 1 (1904).
[4] *Ibid.*, **41**, 1 (1904).
[5] *Zeitsch. f. angew. Chem.*, **21**, 2161, 2209 (1908).

on water at the ordinary temperature is 68 to 69 per cent. of HNO_3. Nitric acid of this concentration has also the highest boiling point at atmospheric pressure and the smallest vapour pressure at ordinary temperatures. In 1908 these authors worked at a temperature of 15° to 18° C., and passed a mixture which originally contained 1 volume of nitric oxide + 2·4 volumes to 2·5 volumes of 88 per cent. oxygen through nitric acid at a velocity of 2·5 litres of nitric oxide per second, with the result that they obtained a nitric acid of 69 per cent. HNO_3. The excess of oxygen was very considerable (after oxidation there was still present 1·7 volumes of oxygen per 1 volume of nitrogen dioxide); thus the excess of oxygen was about 7 times as much as is necessary for the conversion of 1 molecule of the dioxide into nitrogen pentoxide. With gas velocities of 0·4 to 0·5 litres of nitric oxide per hour at 15° to 18° C., the following limiting concentrations were found :—

Percentage of NO in gaseous mixtures.	Percentage of HNO_3 in the resulting nitric acid.
1·0	42
5·0	55

These limits are not ordinarily attained on the manufacturing scale. The reaction gases from arc furnaces containing 1 per cent. of nitric oxide are usually converted into a 30 per cent. acid, and those from ammonia oxidation units containing 7 per cent. of nitric oxide yield at most a 50 per cent. acid, these concentrations corresponding to 22° to 22·5° Bé. and 34·6° to 35° Bé. Foerster and Koch recognised that with more dilute acid and a lower gas velocity a stronger nitric acid can be obtained, but the general view which they expressed was in accordance with that reproduced at the commencement of this paragraph.

The error made by them, which was due to the fact that they generalised the results obtained by them with perfectly definite gas velocities and concentrations of nitric oxide, was explained in German Patent 249,328 (1911) of the Höchster Farbwerke. This patent specification makes the following statement: "Contrary to what has hitherto been held to be technically and theoretically possible, a process has been found of obtaining nitric acid of 70 per cent. concentration and over at the ordinary atmospheric pressure directly from nitrogen dioxide or tetroxide, water and oxygen." It was found that by increasing the concentration of nitrogen dioxide the reaction velocity in the sense of the equation—

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

was raised, whilst simultaneously the evaporation of nitric acid,

which hinders the concentration of the product, was much reduced by decreasing the large excess of oxygen.

According to German Patent 304,322, of 1916, published on December 19th, 1919, the Chem. Fabrik Griesheim-Elektron washes the nitrous gases from the oxidation of ammonia in counter current with hot 50 per cent. tower acid, and thus obtains a 67 per cent. acid. This is, however, purely a concentration process.

In order to explore the phenomena thoroughly, F. Foerster, Th. Burchardt,[1] and E. Fricke [2] carried out a large number of experiments in order to investigate the influence of a mixed stream of nitric oxide and oxygen on aqueous nitric acid, and the reaction between liquid nitrogen dioxide or tetroxide, oxygen and strong acid. Nitric oxide was prepared, of 97 to 98 per cent. purity, from ferrous sulphate, sodium nitrate and sulphuric acid. The oxygen was obtained from cylinders, and had an average strength of 96 to 97 per cent. The earlier results were first confirmed with a mixture containing nitric oxide and oxygen in the proportions of 1 to 2·5, and a gas velocity of 2·4 to 2·5 litres of nitric oxide per hour—that is, 7·2 litres per hour of the total gaseous mixture. The results were as follows :—

Nitric Acid in Receiver.

Original concentrations.	Final concentrations.
40·21 per cent. HNO_3.	44·64 per cent. HNO_3.
45·00 ,, ,,	49·35
49·76 ,, ,,	54·13
55·27 ,, ,,	58·41
60·08 ,, ,,	62·15
64·77 ,, ,,	65·68
69·86 ,, ,,	70·22

The results are, however, different if greater concentrations of nitric oxide are employed, together with lower gas velocities. When using nitric oxide and oxygen in the proportions 1 to 0·75 at a temperature of 15° C. and 1 litre of nitric oxide per hour, and a total of 10 litres of the latter gas, the following alterations in the concentration were obtained :—

Nitric Acid in Receiver.

Original concentrations.	Final concentrations.
64·84 per cent. HNO_3.	70·73 per cent. HNO_3.
70·49 ,, ,,	72·94 ,, ,,
73·20	74·32 ,, ,,
74·79	75·75 ,, ,,
76·01	76·43 ,, ,,
77·01	77·22 ,, ,,
79·94	79·92

[1] See also "Dissertation" (Dresden, 1915).
[2] *Zeitsch. f. angew. Chem.*, 1920, i., 113 *et seq.*

Even with still more concentrated gaseous mixtures, however, acids containing 79 to 80 per cent. of HNO_3 can only be obtained with much slower gas velocities and with very poor yields. An acid of 87·3 per cent. strength, when treated with a gaseous mixture containing 1 volume of nitrous oxide to 1 volume of oxygen, already shows slight reduction in the concentration, due to evaporation and so forth. In all these processes the presence of nitrous acid is indicated by green coloration of the acid. That concentration of acid at which the green coloration is replaced by the purely brown coloration of nitric acid varies according to the proportions of the gaseous mixture employed: with 1 volume of nitric oxide to 2·5 volumes of oxygen it is 62 per cent., and with 1 volume of nitric oxide to 0·75 volumes of oxygen it is 65 per cent., whilst when equal volumes of nitric oxide and oxygen are employed it is 70 per cent. HNO_3.

From the investigations of A. Naumann,[1] E. and L. Nathanson,[2] and F. Haber [3] the following results are deduced for the gaseous mixtures resulting from mixtures of nitric oxide and oxygen at 15° C.:—

Percentage volumes.	N_2O_4.	NO_2.	O_2.	N_2.
$NO : O_2$ = 1 : 0·75 .	48·0	17·5	28·4	6·1
,, = 1 : 1 .	35·9	15·9	43·5	5·4
,, = 1 : 1·5 .	23·6	12·3	59·5	4·6
,, = 1 : 2·5 .	13·6	9·3	73·1	4·0

These results can be approximately confirmed experimentally.

From their experimental results and theoretical considerations, Foerster and his associates compiled the following table:—

Original proportion of nitric oxide to oxygen	Partial pressure as a percentage of the total pressure.		Percentage of peroxide dissolved in:—					
			65 per cent. HNO_3		69 per cent. HNO_3.		75 per cent. HNO_3.	
	As peroxide.	As N_2O_4	Found.	Calculated.	Found.	Calculated.	Found.	Calculated.
1 : 0·75	65·5	48·0	11·39	14·58	15·23	15·70	17·46	22·01
1 : 1·00	51·1	35·9	10·26	10·90	12·01	11·75	16·34	16·47
1 : 1·50	35·9	23·5	7·06	7·17	7·63	7·72	11·28	10·83
1 : 2·50	22·9	13·6	4·13	(4·13)	4·45	(4·45)	6·24	(6·24)

[1] *Liebigs Ann.*, Suppl. VI., 205 (1868).
[2] *Wied. Ann.*, **24**, 454 (1885); **27**, 606 (1886).
[3] "Thermodynamik technischer Gasreaktionen," p. 133; see also W. Nernst, "Theoret. Chemie," 7th edit., p. 687, and K. Schreber, *Zeitsch. f. physik. Chem.*, **24**, 651 (1897).

Nitrogen tetroxide is probably much more soluble than the dioxide, and the final formation of nitric acid may be considered to be due to the reaction—

$$N_2O_4 + H_2O \rightleftarrows HNO_3 + HNO_2,$$

with secondary decomposition of the nitrous acid.

In order to obtain the greatest possible concentration of acid it is, therefore, desirable to add the peroxide to the nitric acid in liquid form. Liquid nitrogen peroxide can be obtained as a brown liquid by oxidising the monoxide with oxygen and cooling with a mixture of ice and salt. Seventy-seven per cent. nitric acid quickly dissolves 10 per cent. of the liquid dioxide. For the experiments acids containing 75–79 per cent. of HNO_3 were used, and were treated with about 20 per cent. of the liquid dioxide. Oxygen was then slowly passed through this mixture or solution. At 10° C., and with an oxygen current of 0·3 litre per hour, the following results were obtained :—

Original absorption acid.		After 48 hours.			After 96 hours.			Percentage of HNO_3 in the resultant acid.
HNO_3 Per cent.	Peroxide Per cent.	HNO_3 Per cent.	Peroxide Per cent	Percentage yield of peroxide.	HNO_3. Per cent.	Peroxide. Per cent.	Percentage yield of peroxide.	
74·98	20·69	76·33	10·36	17·66	76·73	4·93	6·67	76·60
75·69	17·66	76·77	7·72	17·82	76·94	3·75	2·85	76·81
78·81	20·72	79·70	13·14	4·54	79·26	8·48		79·39

The proportion of peroxide used for increased nitric acid formation is very small. In spite of the cooling, the oxygen current removes such quantities of peroxide that these are considerably greater than the proportion converted into nitric acid. Special mechanical mixing of the solution with oxygen appears to be indispensable if favourable yields of nitric acid are to be obtained.

If, for example, 8 gm. of 79·8 per cent. nitric acid are well shaken for four hours with 2 gm. of nitrogen peroxide and 1 litre of oxygen gas, an acid is obtained containing 81·8 per cent. of HNO_3, 20 per cent. of the nitrogen peroxide being effectively utilised. The most interesting experiments are those using such quantities of peroxide as would theoretically suffice to convert all the remaining water into nitric acid.

Pascal and Garnier [1] have made the following determinations of the mutual solubilities of nitric acid and nitrogen peroxide :—

[1] *Bull. de la Soc. Chim.* (4), **25**, 315 (1919).

Solubility of:—

Nitrogen peroxide in anhydrous HNO_3. (Lower layer.)		Anhydrous HNO_3 in nitrogen peroxide. (Upper layer.)	
− 11° C.	48·0 per cent.	− 13·25° C.	2·75 per cent.
− 0·8° ,,	50·0 ,,	− 5° ,,	4·20 ,,
+ 15° ,,	55·0 ,,	+ 5° ,,	5·20 ,,
+ 20° ,,	55·7 ,,	+ 19·5° ,,	7·15 ,,
+ 35° ,,	62·5 ,,	+ 40° ,,	10·00 ,,
+ 50° ,,	70·0 ,,	+ 55° ,,	20·00 ,,

At 56° C. a mixture is obtained of 22·5 per cent. HNO_3 and 77·5 per cent. nitrogen peroxide at the critical point of complete mutual solubility. Above 56° C. only are the liquids miscible in all proportions. Below the boiling point of nitrogen peroxide—that is, below 22° C.—two layers are formed if 60 or more parts of the peroxide are shaken with 40 parts of pure nitric acid. If the acid contains water the solubility of nitrogen peroxide in it is reduced.

Of the layers which are formed on mixing liquid nitrogen peroxide with nitric acid, the upper layer often contains much higher concentrations of nitric acid than the lower. The Höchster Farbwerke, in their German Patent 296,908,[1] published on March 3rd, 1917, give the following example:—

"Fifteen parts by weight of 81 per cent. nitric acid are shaken with 30 parts by weight of liquid nitrogen peroxide; two layers are formed. After the excess of nitrogen peroxide has been blown off from the upper layer, an acid remains containing 98 to 99 per cent. of HNO_3, whilst the lower layer similarly yields an acid containing only 75 per cent. HNO_3." According to this statement, there would be 3·83 parts of 98·5 per cent. acid in the upper layer and 11·17 parts in the lower layer. The water is distributed to the extent of 0·06 parts in the upper layer and 2·79 in the lower layer.

By using nitrogen peroxide in excess the speed of the reaction is greatly increased, as the peroxide tends to remove nitric acid, which would otherwise react as follows:—

$$3HNO_3 \,.\, H_2O \rightleftarrows HNO_3 \,.\, 3H_2O + 2HNO_3.$$

The Höchster Farbwerke treat a mixture of 400 parts by weight of 66 per cent. nitric acid and 1,600 parts by weight of nitrogen tetroxide with oxygen in a vessel provided with a stirrer and reflux condenser. After removing the excess of nitrogen peroxide from the upper layer, an acid of almost 100 per cent. concentration remains, whilst the lower layer, when similarly treated, leaves an acid of 92 per cent., both together providing an acid of about 95 per cent.

[1] The corresponding U.S. Patent 1,180,061 is taken out in the names of Moest and of Nitrum A.G. Zürich.

This figure is confirmed by the experiments of Foerster and his associates. It is advantageous to maintain a low reaction temperature. It is easily possible in this manner to convert tower acid, as obtained from nitrogen oxides, into quite concentrated nitric acid with the help of liquid nitrogen peroxide and oxygen in a few hours.

Thus the following methods are now available for the concentration of 68 to 70 per cent. tower acid :—

(1) The abstraction of water by distillation with sulphuric acid—for example, by the ingenious and satisfactory process of the brothers Pauling.

(2) By treating the nitrous gases with ozone, which is, however, very expensive ; and

(3) By strongly cooling the nitrous gases until liquid nitrogen dioxide or tetroxide separates, and mixing the dilute acid with this and with oxygen at low temperatures and with effective stirring.

F. Foerster, Th. Burchardt and E. Fricke [1] come to the following conclusions :—

(1) The opinion formed as a result of previous experiments, that the production of nitric acid from gaseous nitrogen peroxide, oxygen and water cannot proceed beyond the formation of a solution of nitric acid of minimum vapour pressure, is erroneous.

(2) The reaction velocity in nitric acid of minimum vapour pressure is so small that an enrichment of the nitric acid beyond this point requires a considerable reaction period.

(3) Such enrichment is favoured by as small as possible an excess of oxygen, and by a low velocity of the gas current containing oxygen and nitrogen peroxide.

(4) By continuing the experiment for a sufficiently long period, and by utilising decreasing proportions of the nitrogen peroxide a concentration of HNO_3 exceeding 80 per cent. can scarcely be attained, even under the most favourable conditions.

(5) The reason for this fact is that when gas currents are used the most favourable conditions for the utilisation of the peroxide, namely, a small excess of oxygen and a small gas velocity, are very unfavourable for the thorough mixing of the solution with oxygen, which is also necessary.

(6) It is therefore easy to attain higher concentrations, and even the highest concentrations of nitric acid, by mixing more dilute solutions with the necessary quantity of liquid

[1] *Zeitsch. f. angew. Chem.*, 1920, i., 113–132.

nitrogen peroxide and by shaking or stirring the resulting mixture thoroughly with oxygen.

(7) As was first stated in a patent of the Höchster Farbwerke, reaction occurs especially rapidly if the excess of liquid nitrogen peroxide is so large that the non-homogeneous character of the liquid mixture is ensured by the limited miscibility of the liquid nitrogen peroxide with nitric acid, and that this non-homogeneity is maintained during the reaction.

(8) When nitrous gases react with water, the substance resulting from the equilibrium $2NO_2 \rightleftarrows N_2O_4$, which dissolves in the water, is essentially nitrogen tetroxide, which reacts according to the equation :—

$$N_2O_4 + H_2O = HNO_3 + HNO_2.$$

(9) The decomposition of the nitrous acid so formed, with formation of nitric acid and nitric oxide, and the rapid oxidation of the latter by oxygen, enables the nitrous gases to be converted into nitric acid of the highest concentrations.

In the United States the improvement of methods of absorption of nitrogen oxide has been especially studied by Taylor, Capps and Coolidge of the Bureau of Mines.[1] They succeeded in retaining 85 per cent. of the nitrogen oxides with three towers only, fed with dilute nitric acid. Two further towers retained a further 10 per cent. On increasing the velocity of the gas current from $1\frac{1}{4}$ to $2\frac{1}{4}$ and 4 cu. ft. per minute respectively the absorption fell from 98 to 95 and 91 per cent. respectively, but the nitric acid obtained rose from 23 to 44 and 68 lb. respectively per twenty-four hours. The velocity of the gas current should in no case be too low. The excess of oxygen should never fall below 5 per cent., but, on the other hand, it should not be too high, as otherwise the mixture becomes too dilute. In the latter case large quantities of very fine acid fume are formed, which is difficult to condense and escapes from the towers. The loss of acid can be greatly reduced by the use of the Cottrell process, by which means the last traces of fume are precipitated. The use of electrostatic processes for such purposes is rapidly extending in the United States with favourable results. It is, however, found that in such cases the Cottrell process does not serve so well as it does in the removal of dust from gases, which are contaminated with coarser material. The tower space for the condensation must always be sufficiently large, and the spraying

[1] *J. Ind. Eng. Chem.*, **10**, 270 (1918) ; *Chem. Zentralbl.*, 1920, iv., 388.

should be very intensive, and should be assisted by the use of so-called atomisers.

F. G. Donnan and Irvine Masson [1] have published communications on the theory of scrubbing towers with internal fillings, which were preceded by communications by Partington and Parker [2] which dealt with the special case of the absorption of nitrous gases by dilute nitric acid; the latter workers arrived at certain conclusions which could not, however, be generalised. Starting from certain simplifying assumptions Donnan and Masson established mathematical equations for the erection and working of scrubbing towers. High absorption efficiency depends on a large surface of contact between the gas and the liquid, and within certain limits on a rapid relative motion between these two components. Adeney and Becker [3] have also dealt with the same subject.

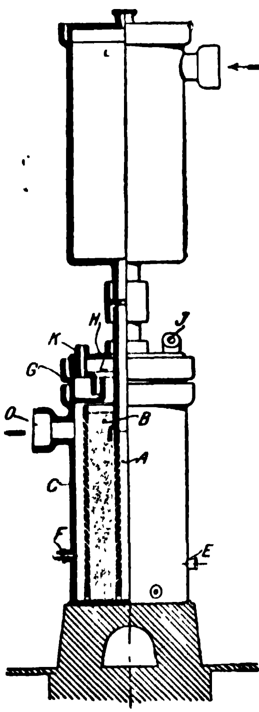

FIG. 65.

According to L. Maugé,[4] an efficient absorption tower should offer the greatest possible surface of contact in the smallest space. Ign. Mościcki [5] has published detailed considerations on suitable plants for the absorption of large quantities of gas. Mościcki first used a small glass absorption vessel filled with glass beads, down which the washing liquid and the gas passed in the same direction. After he had established relations with the Neuhausener Aluminiumgesellschaft, in 1908, Mościcki applied this principle to the absorption of the reaction gases from a 60-h.p. furnace, supplying 6 cu. m. of gas, containing 2·5 per cent. of nitric oxide, per hour, which had to be converted in that time into 50 per cent. nitric acid. For this purpose seven glass towers, each of 200 mm. diameter, were found sufficient.

The absorption towers were further improved as a result of work in the first experimental plant at Vevey and at a laboratory at Freiburg in Switzerland. The towers used at that time in the experimental plant at Freiburg worked as follows:—

[1] *J. Soc. Chem. Ind.*, **39**, 236 (1920).
[2] *Ibid.*, **38**, 75 (1919).
[3] *Phil. Mag.* (6), **38**, 317.
[4] *Ind. Chimique*, **6**, 40 (1919).
[5] *Metan.*, **1**, 61 (1917); *Chim. et Ind.*, **2**, 1303 (1919); *Chem. Zentralbl.*, **1909**, i., 1783; **1911**, i., 1618; 1919, iv., 360; 1920, ii., 553.

The gases entered above into the upper empty portion of the towers (Fig. 65), in which oxidation to nitrogen dioxide took place. They then passed through the tube, *A*, which has perforations 1 cm. in diameter. Through these the gas passed into the space between *A* and *B*, the lower half of which is filled with course quartz fragments, and the upper half with finely divided quartz of 0·3 to 0·4 gm. size. The nitrous gases are absorbed during their horizontal passage through this portion. The residual gases pass through similar openings in the wider tube, *B*, and leave the absorber at *D*. The absorbing liquid circulates through *E* and *F* from tower to tower. *G*, *H*, *I*, *K* and *L* are details of the tight-fitting lid. The dimensions of the apparatus are as follows :—

	Cm.
Internal diameter of the outer casing, *C*	60
Diameter of the cylinder, *B*	44
Diameter of the tube, *A*	10

In the first large Chippis plant 2,500 cu. m. of reaction gases containing nitrogen oxides had to be treated per hour. For this purpose Mościcki constructed another tower (Fig. 66) which worked on the same principle. In this case the internal diameter of the outer casing was 144 cm., whilst those of the inner cylinders were 110 and 40 cm. The perforations in the walls of the inner tube were 5 cm. in diameter. The filling layer was 30 cm. thick in the horizontal direction of the gas current; its height was about 5 m., and the total height of the towers about 6 m. Chippis absorption system No. 1 comprises 8 such absorption towers coupled in series. Between each two towers, with the exception of the two first, empty towers of the same dimensions are interposed in which the nitric oxide is oxidised. The first tower continuously supplies an acid containing not more than 40 per cent. of HNO_3.

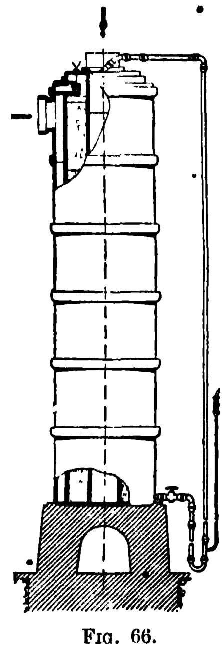

FIG. 66.

Towards the close of 1909 great difficulties arose in the absorption plant just described. In spite of the fact that the centrifugal pump handling the liquid worked excellently, and that there was an ample supply of liquid (more than 50 litres) the effluent gases from the last tower still contained at least 0·3 per cent. of nitric oxide, which corresponded to a loss of 20 per cent.

In order to explain these occurrences Mościcki carried out further laboratory experiments in a tower 3 m. high containing glass cylinders of 20 cm. internal diameter. The following relation exists between the quantity of liquid v, the effective surface of the tower filling in square decimetres, q, and the height of the cylinder, h, in metres :—

$$v = 1 \cdot 1 \times q \times h.$$

This relation must always be fulfilled if the tower is to be fully utilised, and if the effluent gases are to be free from nitric oxide. The necessary volume of liquid is on the average 11 per cent. of the effective space. The water traverses the absorption zone at a velocity of 12·5 cm. per second—that is, each square decimetre of the filling supplies $1 \cdot 25 \times k$ litres of liquid, where k is the proportion of the free space between the filling to the total absorption space. In the special case under consideration, $k = 0 \cdot 5$, which gives a figure of 0·63 litres. In the actual experiment 0·67 litres was found. Generally speaking, it may be stated that the supply of liquid should be so regulated that 0·7 litres of liquid per second pass over each square decimetre of filling surface. The filling always retains considerable quantities of water, as is shown by the following important figures :—

Time in minutes after pouring on the water.	Experimental tower filled with twelve litres of water.		
	Litres of water discharged at the foot of the tower.	Litres of water retained in the tower.	Water retained in c.c. per square decimetre of filling surface.
1	7·20	4·80	53
2	+1·90	2·90	32
3	+0·50	2·40	26
4	+0·20	2·20	24
6	+0·13	2·07	23
9	+0·07	2·00	22
15	+0·12	1·88	21
25	+0·20	1·68	19
	10·32		

Each of the towers at Chippis, already described, contains a space of 3,770 cu. dm. filled with broken quartz, which requires 11 per cent. of that volume, namely, 415 litres of liquid. The effective surface of the filling is 75·4 sq. dm., and therefore the velocity of the liquid should be 53 litres per second. When passing through an absorbing layer 30 cm. in thickness, the gas, travelling at an average velocity of 20 litres per square centimetre surface, undergoes a

pressure drop of 1·6 mm. of water-column, if the quartz particles weigh 0·3 to 0·5 gm. Under the same conditions particles weighing only 0·1 gm. cause a reduction in pressure of 5·2 mm. of water-column. It is therefore advisable to sift the filling in order to obtain a uniform material consisting of particles weighing from 0·3 to 0·5 gm. After the method of working in Chippis had been modified in accordance with these figures, no further losses of nitric oxide occurred in the effluent gas from the towers.

For the later extension of the works at Chippis Mościcki devised another form of tower, which enabled towers to be constructed very cheaply with a considerable saving of material, by simplifying the plant in such a manner that it could be constructed of several large units (German Patent 256,295, U.S. Patent 1,046,212, French Patent 444,027, British Patent 17,355/1911, Swiss Patent 58,406).

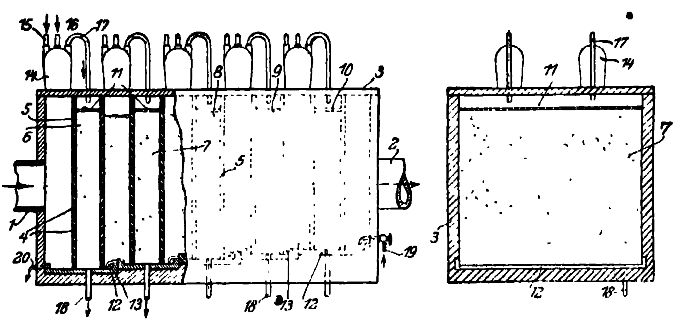

FIG. 67.

These units are constructed of acid-proof masonry, with the help of a cement of asbestos and water glass, and of a special asphalt. The apparatus is represented diagrammatically only in the patent and in the sketches (Fig. 67). It has worked satisfactorily at Chippis for several years. The nitrous gases pass horizontally through a series of chambers, 6, 7, 8, 9 and 10, down which the absorbing liquid trickles, and which are separated from one another by diaphragms, 5, permeable to the gases. The individual chambers may, for example, be filled with broken quartz, which is contained under the perforated sandstone plates, 11. Between these absorption chambers oxidation chambers are interposed which receive no liquid. The acid flowing from the individual chambers is returned through the pipes, 18 and 15, into the pressure pot, 14, in which air pressure is maintained through 16, and which discharges into the next absorption chamber through the U-tube 17. The mains, 19 and 20, and the overflows, 13, serve for the transport of the acid through the whole plant.

Mościcki considers the absorption process to occur according to the following equations :—

$$3NO_2 + 3NO + 3H_2O = 6HNO_2$$
$$6HNO_2 = 2HNO_3 + 4NO + 2H_2O$$

According to Mościcki, by cooling to 100° C. and under, only 50 per cent. of the nitric oxide originally present need be converted into nitrogen peroxide. In the small experimental plant at Freiburg, Switzerland, the first three towers absorbed 80 per cent. of the nitrogen oxides, the two following towers 12 per cent., and the two last towers 6 per cent only. The losses in the effluent gases amounted to 2 per cent. only.

Mościcki comes to the following conclusions :—

(1) The optimum size for the filling material (quartz) is 0·1 to 0·2 c.c. of which size 1 cu. m. corresponds to 600 sq. m. of surface.

(2) The most suitable gas velocity is about 2 cu. m. per hour per square decimetre of filling surface.

(3) The thickness of the absorption layer in the direction of the gas current need only amount to 30 cm.

(4) One cubic decimetre of space occupied by the filling suffices for the absorption of 0·67 cu. m. of gas per hour.

(5) Thirty centimetres of filling layer reduce the gas pressure by 1·6 mm. of water-column at a gas velocity of 2 cu. m. per square decimetre of filling surface.

(6) At least 0·7 litres of liquid should be supplied per second per square decimetre of filling surface.

(7) The total volume of the liquid used for absorption should be at least 11 per cent. of the total volume of the absorption layers.

In opposition to F. Foerster and his associates [1] Mościcki assumes the intermediate formation of nitrogen trioxide during the absorption, or rather the formation of a gaseous mixture which behaves as the trioxide in contact with an absorption agent, whereas the former consider the formation and reactions of nitrogen tetroxide to be alone of importance,

$$2NO_2 \rightleftarrows N_2O_4 \text{ and}$$
$$N_2O_4 + H_2O \rightleftarrows HNO_3 + HNO_2$$

Which group of reactions supplies the main portion of the acid depends essentially on the temperature of absorption. At low temperatures condensation will mainly take place in accordance with

[1] *Loc. cit.*

Foerster's assumptions, whilst with rising temperature the proportion formed by the nitrogen trioxide reaction assumed by Mościcki and others will increase. We know that at above 300° C. the B.A.S.F. obtain pure nitrate, free from nitrite, from nitrous gases by absorption by alkalies (German Patent 188,188).

Apart from the literature already mentioned and discussed, so many patents and publications deal with the recovery and concentration of nitric acid from the nitrous reaction gases of arc and ammonia oxidation furnaces that a selection only of the most important literature can be given here.[1] P. Winand oxidises nitric oxide to the dioxide by the action of concentrated nitric acid (German Patent 186,333) or of a mixture of fused nitrate, nitrite and concentrated sulphuric acid (German Patent 193,696). Chem. Werke vorm. Dr. H. Byk decompose calcium nitrate with sulphuric acid (German Patents 208,143, 217,476). Elektrochemischen Werke G.m.b.H. absorb nitrous gases by weakly basic oxides such as zinc oxide, and heat the salts which are so formed to 500° C. The metallic oxide is regenerated, whilst nitrogen oxides are evolved, which are converted into 40 per cent. commercial acid in towers by the action of water (German Patent 212,423). According to German Patent 249,329 of Farbwerke vorm. Meister, Lucius & Brüning pressure pots for conveying nitric acid may advantageously be actuated by oxygen instead of air. According to German Patent 218,570 of Le Nitrogène S.A., nitrous gases are absorbed by passing them over a mixture of potassium and sodium compounds, with formation of a mixture of potassium nitrate and sodium nitrite. Fr. Bayer & Co.[2] absorb nitrogen oxides by freshly-ignited wood charcoal. C. Schlarb absorbs nitrous gases in water in presence of oxides of iron, aluminium or chromium soluble in nitric acid, and obtains pure nitric acid from the solution by evaporation *in vacuo* (German Patents 243,840, 243,892). Farbwerke vorm. Meister, Lucius & Brüning obtain pure nitric oxide from nitric acid containing nitrogen trioxide by electro-reduction (German Patent 244,362). According to German Patent 246,615, nitrogen oxides are brought into contact with dry halides before absorption.

The Dynamit A.G. vorm. Alfr. Nobel & Co., of Hamburg, absorb nitrous gases by means of amyl acetate, which is regenerated in an air current (German Patent 267,874). U.S. Patent 1,047,576 of W. Schultze and the General Chemical Company describes the production of a solid compound $N_2O_5(SO_3)_4.H_2O$ from nitric and sul-

[1] Compare the periodical reports in the *Chem. Ztg.* and *Uhlands Wochenschrift für Industrie und Technik*, 21, 10–13 (1908).
[2] *Chem. Ztg.*, 1910, "Repertorium," p. 581.

phuric acids. According to U.S. Patent 1,057,052, Ph. A. Guye obtains more concentrated nitrous vapours and nitrogen oxides from dilute gaseous mixtures by special methods. A. Th. Schloesing (French Patent 460,328) brings nitrous gases into contact with lime at 300 to 400° C. after the hot gases, at 700° to 800° C., have previously been used for calcining the limestone briquettes. Norwegian Patent 24,195 deals with a proposal of H. A. Wielgolaski on the concentration of nitrate solutions as obtained by the absorption of nitrogen oxides.

German Patent 261,027 and Swiss Patent 57,534 of the Elektrochemischen Werke G.m.b.H. and F. Rothe deal with the recovery of pure nitrites from nitrous waste gases and alkalies. French Patent 411,674 and German Patent 238,369 of the B.A.S.F. describe a process of obtaining pure nitrates from mixtures of nitrate and nitrite. Meister, Lucius & Brüning obtain pure nitric oxide and nitrogen peroxide by the electrolysis of nitric acid (British Patent 10,522/1911 ; see also Swiss Patent 57,047).

Ch. Torley and O. Matter decompose ammonium nitrate by heat, forming nitrous oxide (British Patent 11,828/1913). In order to recover nitrous acid from very dilute nitrous gases, for example from the residual gases from absorption towers, with a fine spray of water, C. Rossi (French Patent 463,825) passes the gases between two aluminium plates maintained at a potential difference of 20,000 to 40,000 volts. One of these aluminium plates is smooth, whilst the other is provided with prominences, for example, of asbestos. The water spray, together with the nitrogen oxides, is precipitated electrostatically and acid of 36° to 42° Bé. is so recovered. According to French Patent 563,830, dilute acids can be concentrated to 42° Bé. in a vacuum pan of acid-proof material.

In German Patent 269,656, Traine & Hellmers, E. Weyer and Fr. Brandenburg claim the decomposition of calcium nitrate with formation of lime and nitrogen oxides under certain defined conditions in an ordinary calcining furnace.[1]

According to German Patent 284,042 of the Norsk Hydro, lime briquettes for the direct absorption of nitrous gases at 300° to 400° C. should be produced by burning limestone at a temperature not exceeding 700° to 750° C., as otherwise the absorption capacity of the product is much reduced. In German Patent 300,897, the same firm illustrates by an example a combined absorption and concentration process. The vapours obtained by boiling 67 to 68 per cent. nitric acid, of boiling point 125° C., are mixed with oxygen and led into a glass column, filled with broken quartz, which is 140 cm.

[1] See also French Patent 457,800.

high and of 4 cm. internal diameter ; down this column there is passed a nitrous-sulphuric acid of the following composition :—

35·7	per cent.	$HNSO_5$
56·8	,,	H_2SO_4
2·5	,,	HNO_3
5·0	,,	H_2O

The mixture of nitric acid, nitrogen dioxide and oxygen which escapes from the top of the column is passed through a condenser in which red fuming nitric acid condenses, whilst the uncondensed gases pass on and are recovered in the form of 65·7 per cent. nitric acid in a final tower fed with water. The red fuming nitric acid from the condenser is distilled under a dephlegmator, and nitric acid of 95·7 per cent. concentration containing 0·4 per cent. of nitrogen peroxide only is thus obtained. The nitrogen oxides which are distilled off pass through the above-mentioned condenser to the absorption tower. The glass denitration column is maintained at a temperature of 65° C. above, and 164° C. below. The discharged sulphuric acid, which contains 78·8 per cent. H_2SO_4, is free from nitrous gases, and contains 1·05 per cent. of nitric acid only. German Patent 318,691 of the Norsk Hydro is similar. According to this latter patent, the dilute nitrous gases are absorbed in 90 per cent. sulphuric acid, as the solubility of nitrosyl sulphuric acid in sulphuric acid decreases with the concentration of the latter ; its solubility in 83 per cent. sulphuric acid is, for example, only one-third of that in 91 per cent. acid. The mixture which is obtained, containing nitrosyl sulphuric acid, is denitrated by distilling through a dephlegmator. According to French Patent 465,740 of the Norsk Hydro process, the process is recommended of neutralising 30 per cent. acid with limestone, returning the liquid so obtained to the top of the towers, re-neutralising and so on. Norwegian Patent 30,386 deals with details of the process of recovering nitrogen oxides from the dilute nitrous gases by refrigeration. According to Norwegian Patent 30,512, the Norsk Hydro replaces the rocking crystallisers formerly employed by closed tubular crystallisers. According to Norwegian Patent 30,418, oxidation with nitric acid may be carried out by starting the reaction at a pressure of more than 1 atm. and then maintaining it by injecting oxygen.

In German Patent 306,353 H. Pauling claims a process of absorption of nitrogen oxides produced by the arc process, which is characterised by treatment of the gases with the absorption agent at high and low temperatures alternately. In German Patent 313,338 he describes specially adapted sieve-plates for

absorption towers and further improves the design in German Patent 323,296.

German Patent 304,322 of Chem. Fabrik Griesheim Elektron, already described, was followed by German Patent 305,122 of the same firm, in which an absorption and concentration tower is described the internal portion of which is surrounded by a protective space.

German Patent 302,533 of H. Petersen states that the absorption of nitrogen oxides proceeds more smoothly if the components, which in this case are nitrous gases and steam, are passed through the system in the same direction instead of in opposed directions, as in the present method of scrubbing with water. In German Patent 307,312 a special atomiser is recommended, whilst in German Patent 312,023 suitable filling bodies are described.

When furnace gases containing nitrogen oxides are refrigerated, liquid nitric acid condenses, which prevents the use of metallic condensers under certain circumstances. According to German Patent 304,002, J. Straub therefore adds sulphur dioxide or trioxide to the gases, in which case sulphuric acid is precipitated, which is much less injurious, enabling wrought-iron apparatus to be used. This complicated process is now avoided by using acid-proof alloys for the construction of such condensers. A special arrangement of towers is claimed in German Patent 321,614 of Smith's Patent Vacuum Machine Co., Ltd. In German Patent 323,295 H. Frischer claims the use of a hood with the washing and rectifying columns, and in German Patent 323,474, jointly with M. Drees, he claims an apparatus and process for the treatment of gases and vapours with liquids. According to British Patent 121,039/1918 and German Patent 325,637, K. B. Quinan claims the use of intermediate diaphragms in order to attain intimate contact between liquids and nitrogen oxides.

For the filling of absorption towers, apart from the various forms of filling already mentioned, Raschig rings [1] of porcelain, stoneware, and so forth, have proved very successful. They are protected by German Patents 286,122, 289,121, 292,622, 297,379; Belgian Patents 268,956 and 271,344; Danish Patents 22,049, 22,273 and 22,444; British Patent 6,288/1914; Dutch Patent 1,715; Norwegian Patent 28,121; Rumanian Patent 3,968; Russian Patent 64,421; Swiss Patents 69,764, 73,885 and 73,886; Hungarian Patent 68,318; and U.S. Patent 1,141,266. These rings offer a very large surface with very small resistance to the gas current. With a filling height of 1 m. and a gas current of 1 m. per second, the pressure caused by

[1] *Chem. Ztg.*, 1920, pp. 122–123.

these rings is less than 20 mm. of water-column. A pressure of 10 mm. only suffices to pass 20,000 cu. m. of gas in twenty-four hours through a Raschig tower 10 m. high and of 1 sq. m. cross section. A gentle flow of liquid over the rings scarcely affects the pressure difference. When more than 2 cu. m. of liquid are added per square metre cross-section per hour, the back pressure is higher. With 6 cu. m. the pressure is doubled at a gas velocity of 1 m. per second, and with 10 cu. m. and a gas velocity of 1 m. per second choking occurs.

Among other forms of filling we may mention the flat rings of Prym & Co., Stolberg, Rhineland (German Patent 317,166/7), and the so-called S-rings of A. Landgräber, Berlin. Filling bodies are also described in German Patents 314,597, 316,497, 316,594 and 321,078.

K. Rosenstand-Wöldike[1] decolorises concentrated sulphuric acid, coloured by nitrogen oxides, by the addition of hydrogen peroxide. We cannot enter here into the important practical question[2] of the denitration and recovery of mixtures of nitric and sulphuric acids (German Patents 297,902, 303,396, 313,046 and 323,416).

With the extension of the nitric acid industry, cases of nitric oxide poisoning have accumulated.[3] In works, the danger of brown vapours should continually be insisted on.

The gas washers of the firm of Eduard Theisen, Munich, have been recommended for the absorption of nitrous gases and for other uses, but have not so far attained much importance for this particular purpose.

On the other hand the absorption towers of Steuler & Co., G.m.b.H., Coblenz, are widely used.

Fig. 68 shows sections and plans of a three-tower battery according to this system. Each tower has its accompanying storage vessels and acid-proof rotary pumps, which transport the washing liquid to a stoneware storage vessel on the top of the tower. From this the liquid flows to a stoneware sprinkler—namely, an "Effektor" of the Deutsche Steinzeugwarenfabrik, Friedrichsfeld-i.-Baden. The "Effektor" distributes the liquid in a regular stream over the whole cross-section of the tower.

The Steuler towers are constructed of acid-proof stone and acid-proof cement. Within, a grid supports the tower-filling, consisting of Raschig rings or other suitable filling bodies. In order to absorb the heat caused by the absorption of the nitrogen oxides in water or

[1] *Chem. Ztg.*, 1920, p. 255.
[2] *E.g.*, *Chem. Ztg.*, 1919, p. 805, "Repertorium," p. 255; *Chem. Zentralbl.*, 1919, iv., 430.
[3] *Chem. Ztg.*, 1917, "Repertorium," pp. 41, 178.

dilute acid, coolers are often interposed between these towers, and are constructed of ferro-silicon, V2A-metal or other suitable material.

Fig. 69, representing the absorption plant at Tubize (1913), shows the whole arrangement clearly ; five Steuler towers in series follow the rectangular oxidation chamber. In this installation the pumps

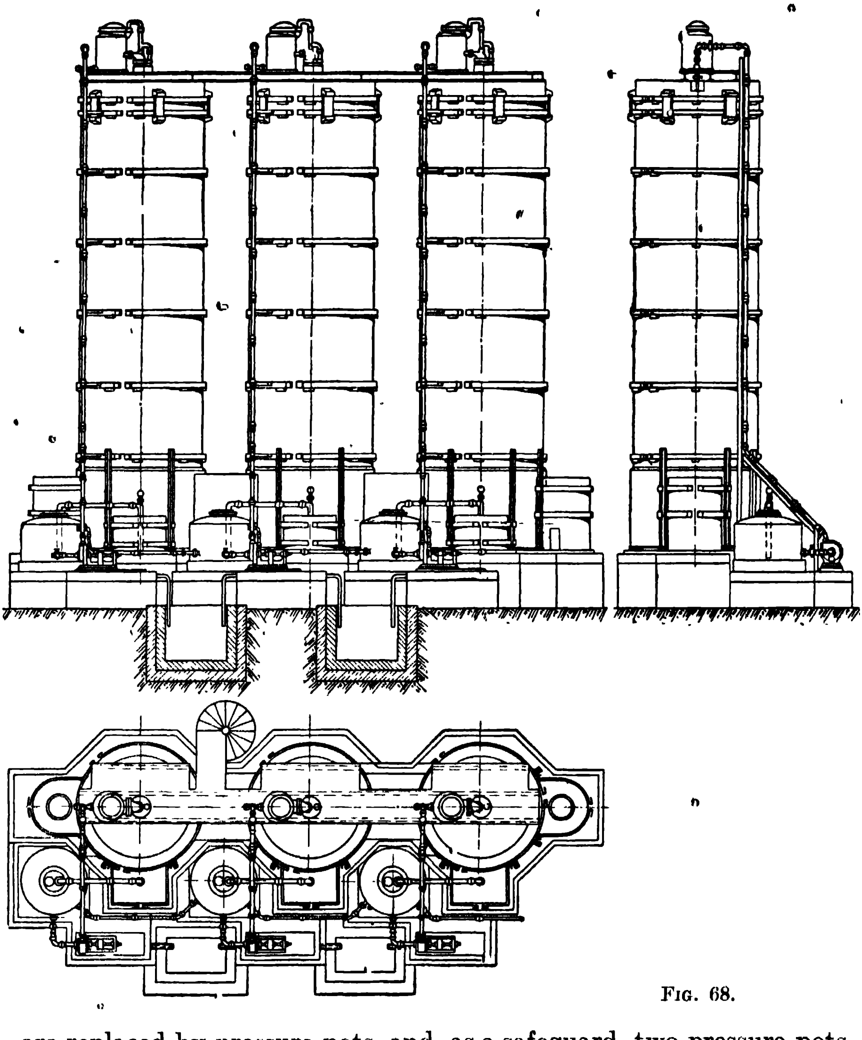

FIG. 68.

are replaced by pressure pots, and, as a safeguard, two pressure pots and two automatic elevators are provided for each tower.

Acid-proof alloys [1] are of great importance in the manufacture of nitric acid, for it is obviously better and safer to work with metal plant than with stoneware or silica. In the United States the alloys,

[1] *Chem. Zentralbl.*, 1919, ii., 917 ; iv., 174, 183, 909 ; 1920, ii., 726 ; *Metallbörse*, 1921, p. 262.

duriron, tantiron and ironac are largely employed, in France, métillures, and in Italy, etianit, all of these being ferro-silicon alloys. O. L. Kowalke [1] tested various alloys of this class with regard to attack by 10 per cent. solutions of sulphuric, hydrochloric, nitric,

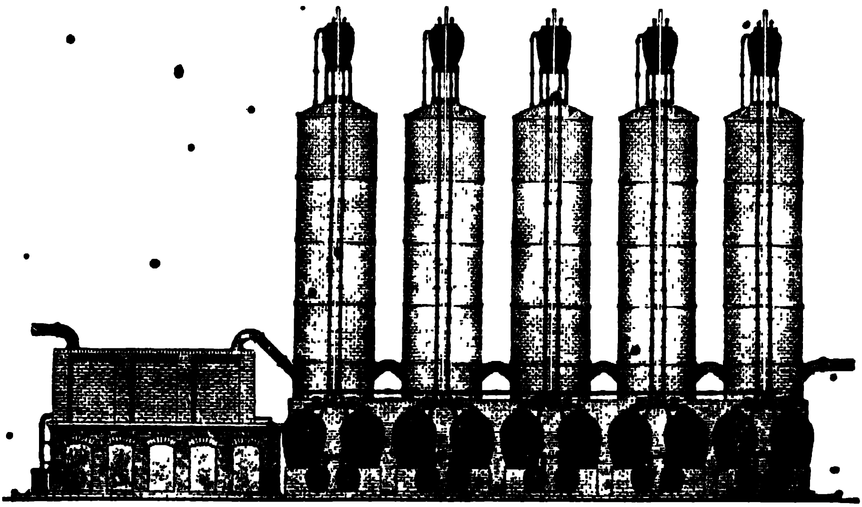

Fig. 69

acetic and citric acids, and found that the resistance to corrosion was least when 1·2 to 3·3 per cent. of Si was present, and greatest when the alloys contained 16 to 18 per cent. Unfortunately these alloys are very hard and brittle.

A German acid-proof alloy (fragment of a tube) gave the following figures on analysis :—

77·09 per cent. Fe ; 18·23 per cent. Si ; 3·79 per cent. Mn ; 1·39 per cent. Al ; and 0·155 per cent. P.

C. Matignon [2] gives the following figures :—

Name of Alloy.	Si Per cent	Fe Per cent	Mg Per cent	Al Per cent.	C Per cent	P Per cent	S Per cent	Ni Per cent
Métillure (French) .	16·92	81·05	0·88	0·25	0·592	0·173	0·01	—
Etianit I. (Italian) .	15·07	82·40	0·62	—	—	—	—	—
Etianit II. (Italian) .	15·13	80·87	0·53	—	0·82	0·06	0·03	2·23
Ironac (American) .	13·16	83·99	0·77	—	1·08	0·78	0·05	—
Duriron (American).	15·51	82·23	0·66	—	0·83	0·57	0·01	—

All the above-mentioned alloys are attacked by hydrochloric acid. Apparatus of tantiron,[3] which is similar to duriron, is manufactured,

[1] *Proc. Amer. Electrochem. Soc.*, 1917, May 2nd to 5th ; *Zeitsch. f. angew. Chem.*, 1918, ii., 18.
[2] *Chem. Ztg.*, 1918, p. 453.
[3] *Chem. Zentralbl.*, 1919, iv., 174.

amongst others, by the Tantiron Foundry, Glenville Grove, London, S.E. 3. The addition of nickel always increases the resistance to acids.[1] In cast-iron apparatus [2] the skin of the casting acts as a temporary protection against attack by acids. Concentrated sulphuric and nitric acids do not attack iron; aluminium is also fairly resistant to concentrated nitric acid. In German Patent 319,465 Gebr. Siemens & Co. claim the use of moulded bodies of silicon carbide. According to German Patent 319,475, a few tenths of a percentage of nitric acid render nitrosyl-sulphuric acid inert towards iron.

In Germany ferrosilicon castings are supplied amongst others by the Freier Grunder Eisen und Metallwerke G.m.b.H., of Neunkirchen-nr. Arnsberg; the Iron Foundry and Engineering Works Julius Römheld, Mayence; Baum A.G., Herne in Westf., and Maschinenfabrik Esslingen A.G., Esslingen-a.-Neckar, which supplies the extremely resistant alloys Thermisilid and Esilit. Similar products of Friedr. Krupp A.G., Essen, are also very important. Their V2A-metal is a chrome-nickel steel, and has the following mechanical properties :—

Breaking strain in kilograms per square millimetre	38
Tensile strength in kilograms per square millimetre	80
Elongation per cent.	40
Resistance to impact in kilograms per square millimetre	25

It offers no difficulties to mechanical working and can be welded autogenously. It is therefore widely used for the manufacture of piping, condensers, nitric acid pumps, valve seatings, valves, plungers, pistons, stirring blades and so forth. The high breaking strain even at high temperatures and the excellent resistance to attack by rust, sea water and nitric acid (but not to sulphuric and hydrochloric acids) are shown by the following table :—

Temperature.	Breaking Strain Kilograms per square millimetre.	Tensile Strength Kilograms per square millimetre.	Elongation. Per cent.	Contraction Per cent.
20° C.	38	79·4	46·4	54
200° C.	31	75·3	55·5	55
300° C.	26	70·2	47·0	54
400° C.	25	63·8	40·5	50
500° C.	24	58·3	22·4	47
600° C.	18	56·6	26·0	34

[1] *Metallbörse*, 1920, p. 674.
[2] *Chem. Zentralbl.*, 1919, iv., 825; *Chem. Ztg.*, 1919, *Chem. Techn. Übers.*, p. 163; *Ber.*, **34**, 4090 (1901).

	Rusting in the air. Loss of weight.	Corrosion in sea water. Loss of weight.		In nitric acid (10 per cent. cold). Loss of weight.	In 50 per cent. nitric acid. Boiling. Loss of weight.
Cast iron . . .	100	100	Cast iron . . .	100	100
9 per cent. nickel steel.	70	79	5 per cent. nickel steel.	97	98
25 per cent. nickel steel.	11	55	25 per cent. nickel steel	69	103
V2A metal . . .	0	0·6	V2A metal . .	0	0

V2A rustless steel, is also very resistant to the action of gases and vapours at high temperature, as is shown by the following figures :—

On heating samples in a furnace with excess of air at 1,000° C., the loss in weight in 100 hours was 416 g. for cast iron ; 6 g. for V2A metal.

On heating samples in a furnace with excess of air at 1,200° C. for 25 hours, the loss of weight was 250 g. for cast iron and 10 g. for V2A metal.

V2A metal is particularly suitable in practice when used with the strongest cold acid. At 60° C. it is somewhat attacked by nitric acid of 26° Bé. V2A metal cannot be tempered, but can be cold-rolled till elastic. In consequence of its great toughness and resistance to shear, this steel has to be worked extremely slowly. In order to maintain its valuable mechanical properties, special heat treatment is necessary for all parts fashioned of V2A metal. V2A metal is entirely non-magnetic. It is particularly useful where a high degree of resistance to the attacks of nitric acid or ammonia is required in simultaneous presence of water vapour.

The Krupp Works supply V2A metal in the form of bars, sheets, vessels, valves, cocks and castings of all kinds. Welded tubing of V2A sheet is supplied by the tube works, G. Kuntze, Bochum-i.-W. ; nitric acid pumps of V2A metal are supplied by Gebr. Sulzer A.G., Ludwigshafen-a.-Rh. and Amag-Hilpert Nürmberg.

Friedr. Krupp A.G. now also supply a special variety of acid-proof ferrosilicon castings on Walter's system, under the name of Thermisilid. In consequence of suitable composition and heat treatment, thermosilid shows a uniform fine structure. It can be used for castings the manufacture of which from ordinary ferrosilicon alloys was impossible. They are far less brittle and breakable than earlier castings of the same kind. Thermisilid is completely resistant to sulphuric acid and nitric acid of all concentrations. Thermisilid castings are also supplied by the Maschinenfabrik Esslingen A.G.

Maschinenbau A.G. Golzern-Grimma, Grimma-i.-Sa., turned its attention to ferrosilicon alloys at an early date. According to

E. Golz [1] this firm was the first to experiment on a large scale with such castings in Germany. "Acidur" has an excellent record in practice—for example, at Höchst and Wolfen. E. Golz enters into the whole question of ferrosilicon alloys in detail, including the many difficulties which had to be overcome in the foundry before satisfactory castings could be manufactured (see, for example, German Patent 277,855). The resistance of acidur to acids was shown by treating fragments of 40 to 60 gm. in weight for 38 hours with boiling nitric and sulphuric acids of various concentrations; 0·02 per cent. was dissolved in nitric acid and 0·04 per cent. in sulphuric acid. On heating a small bar of acidur with 2 per cent. of sulphuric acid in autoclaves at 3 atm. pressure, traces only were dissolved. Fig. 70 shows a condenser for nitric acid manufactured of acidur by the Maschinenbau A.G. Golzern-Grimma.

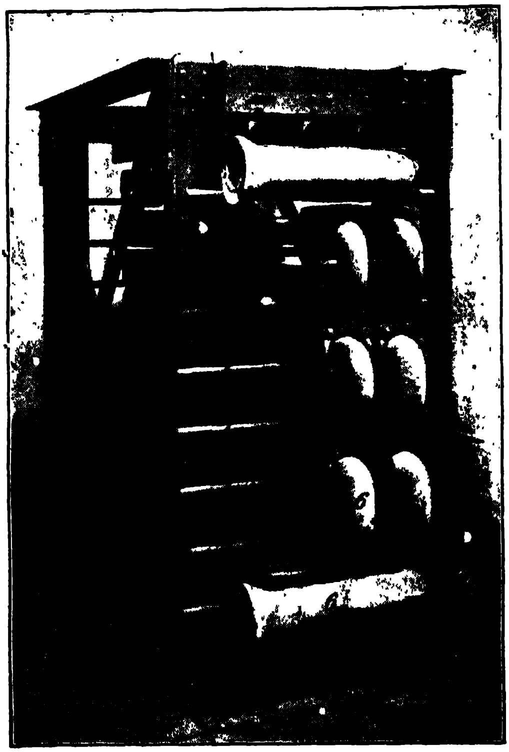

FIG. 70.—Acidur nitric acid cooler, to be sprayed externally.

Whereas stoneware pumps, which were very breakable and inefficient, were at one time exclusively used in the nitric acid industry, these have been replaced by pumps of acid-proof metal during the last few years. Stoneware pumps are, however, still to be recommended for salt solutions.

Very efficient acid pumps are constructed by the Amag-Hilpert Pegnitzhütte, Nürmberg. The manufacture of these special pumps was mainly developed during the War. The Amag-Hilpert Company supply the following types :—

(1) Nitric acid pumps of acid-proof chrome-nickel steel (V2A).

[1] *Chem. Apparatur*, 1917 (4), pp. 145, 169.

(2) Special acid pumps for mixed acid, constructed entirely of cast steel.

(3) Sulphuric acid pumps for concentrated acid; all parts in contact with the acid are constructed of cast iron.

(4) Hard lead pumps for use with dilute sulphuric acid.

(5) Universal thermisilid circulating pumps, which replace all types 1 to 4.

The overhanging bearing-seating is characteristic of all the Amag-Hilpert acid pumps. The stuffing box, the most sensitive part of any acid pump, is free and readily accessible. Should acid pass through the packing, it can be collected in stoneware vessels placed below, without coming into contact with the bed-plate. The stuffing-box itself consists of two separate parts inserted one in the other, so that escape of acid is prevented, by being drawn off through a special port. A further stuffing-box prevents acid from travelling along the shaft. In nitric acid pumps, into which the liquid usually flows at about 1 m. excess pressure, the stuffing-box is protected by the inclusion of a small wheel with axial blades, which prevent acid from reaching the packing of the stuffing-box when the pump is working.

In the nitric acid pumps only one flange packing is necessary at the suction joint. This is so arranged that the suction pipe fits into the pump housing by means of a conical ground joint. The housing is itself flanged to the bearing-seating, and the ground joint sustains 12 atm. pressure. Destructible packings, such as asbestos, asbestos board, and so forth, are therefore not necessary.

The shaft is carried on two lubricated bearings, which are so spaced that the fly-wheel can be adjusted whilst running. One stuffing-box only is required at the seating end. The usual sizes have the following dimensions:—

10 cu. m. per hour.	21 m. head.	Horse-power of motor	5·0
18 cu. m. ,,	25 m. ,,	,, ,,	7·5
30 cu. m. ,,	25 m. ,,	,, ,,	10·0
45 cu. m. ,,	25 m. ,,	,, ,,	12·5

All types are constructed to be driven at 2,800 to 2,900 revolutions per minute with three-phase drive of 50 periods, and direct coupling with the motor. The rated head refers to water. The actual head alters with the specific gravity of the acid. Sulphuric acid and mixed acid pumps are also constructed for large outputs and for 1,450 revolutions per minute. The construction of these pumps is protected by patents and registered designs. The pumps are shown in Fig. 71.

The centrifugal acid pumps of the Wesselinger Gusswerk Hans

Eichler, Wesseling, near Cologne, have also proved quite satisfactory. In these pumps two special alloys are used—namely, wegucit, which is finely grained and of relatively great mechanical strength, and antacid, which is coarser and harder. Tubes, cocks, retorts, pans, boilers, and so forth, are manufactured of these metals.

The Eichler pumps differ from those already described mainly in the construction of the stuffing box. On the suction side no stuffing box is used, and on the pressure side it is so constructed that no packing material is necessary. On the shafts there are two rings of acid-proof material situated close together, which are so con-

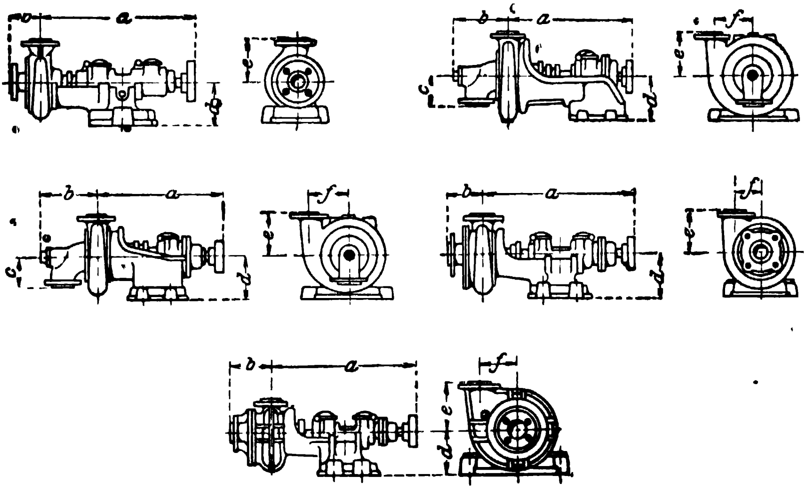

FIG. 71.

structed that they form a sort of labyrinth. Any acid trickling through the slit in the protecting disc is carried by an auxiliary rotary conveyor along a special channel into the suction chamber, so that it cannot escape during working. When the pump is out of action the protective disc is pressed against the housing, thus increasing the action of the labyrinth, and assists in preventing acid from escaping through the stuffing-box. Any acid which may escape in spite of these arrangements is led away through a funnel cast on to the pump itself.

In the following table we reproduce a few figures on one-stage Eichler pumps of the most usual sizes. The head increases in pumps of several stages in accordance with the number of stages. The power requirements are calculated for specific gravity 1, without allowance for viscosity and so forth. These pumps are driven by directly coupled motors or by belt transmission.

Type.	Bore of attached piping.	Revolutions per minute.	1,450	1,800	2,000	2,300	2,400	2,600	2,800	2,900
Hs 125	50 mm.	Output in litres per minute.	—	—	180	210	240	270	285	300
		Manometric head in metres.	—	—	7	10	11	13	15	17
		H.P.	—	—	0·93	1 55	1·95	2·60	3·15	3·80
Hs 150	80 mm.	Output in litres per minute.	260	330	375	400	425	450	480	525
		Manometric head in metres.	6	9	12	14	16	19	22	23
		H.P.	1·15	2·20	3·30	4·15	5	6 30	7 85	9
Hs 175	100 mm.	Output in litres per minute.	410	525	600	650	710	780	800	850
		Manometric head in metres.	8	12	15	21	23	27	31	34
		H.P.	2·50	4·60	6·70	10	12	15·60	18·40	21·40

On "Cerathrem" pumps, see *Chem. Zentralbl.*, 1920, iv., 554.[1]

Apart from the above-mentioned acid-proof alloys, stoneware naturally also plays an important part as a constructional material for towers, piping, certain pumps, fans, automatic pressure pots, and so forth.[2] The construction of towers, chambers and containers of acid-proof stoneware is largely carried out by Tonwerk Biebrich A.G. Schamottefabrik, Biebrich-a.-Rh. German Patent 299,805, of this firm, describes a hollow filling-body for absorption and reaction towers. Tools, pumps, fans, automatic pumps, distributors, and so on, of stoneware, are also supplied by the Deutsche Steinzeugwarenfabrik für Kanalisation und Chemische Industrie, Friedrichsfield, Baden. Very efficient plant is also supplied by the Deutsche Ton und Steinzeugwerke A.G., Berlin-Charlottenburg, who also supply silica (vitreosil) apparatus and tubes. In France silica ware is supplied by the Soc. le Quartz Fondu, l'Argentière-la-Bessée (Hautes Alpes).

Acid towers may also be filled with granite, lava, and so forth, instead of with specially formed filling bodies (see also H. Frischer,

[1] See also German Patent 304,298; *Chem. Ztg.*, *Chem. Techn. Übers*, 1920, pp. 253, 267; *Chem. Zentralbl.*, 1920, iv., 357, 358.

[2] *Chem. Zentralbl.*, 1919, iv., 364; *Verh. d. Ver. z. Bef. d. Gewerbfl.*, 1918, Part VIII., p. 199.

German Patents 324,441, 324,921). The firm of H. Buchmeyer, Herdecke-i.-W., supply silicious natural stone for this purpose.[1]

The problem of devising a satisfactory method of concentrating dilute nitric acid has long been studied.[2] This problem may now be considered to be solved. Not only is the method of the Höchster Farbwerke, already discussed, available, but the admirable process of Pauling has in the meanwhile been so far perfected that it works satisfactorily on a technical scale.

Processes of concentrating nitric acid have been the subject of so many descriptions and patents that we can only describe a selection here of the various methods proposed. The suggestion of C. Übel (German Patent 210,803) to concentrate nitric acid by distillation with sulphuric acid in a special manner was followed by German Patent 236,431 and Norwegian Patent 17,124 of the A.B. Nitric Syndicate, of Stockholm, which first concentrates a 25 to 30 per cent. acid to 60 per cent., and then concentrates the latter further at a second stage by means of concentrated sulphuric acid. We must also refer to the interesting work which is recorded in various patents of O. Boeters, R. Wolffenstein, O. Dieffenbach, C. Übel, and others, on the concentration of dilute nitric acid by the addition of salts with an affinity for water, more particularly of nitrates, sodium sulphate and sodium bisulphate.

French Patents 455,531 and 455,532 deal with the concentration of nitric acid, as do also E. Collet's French Patents 447,106, 450,448. In German Patents 257,809 and 274,165 and British Patent 22,320/1914, H. Pauling describes his first process, according to which dilute nitric acid is concentrated by treating it with sulphuric acid and heating in counter current. French Patent 462,290 of the Verein Chem. Fabr. Mannheim also deals with the concentration of nitric acid by sulphuric acid.

After the outbreak of War, when the explosive works required constantly increasing quantities of concentrated nitric acid, this question was studied still more intensively. According to German Patent 289,745, the Norsk Hydro evaporates the nitric acid to be concentrated, and passes the vapours in counter-current to concentrated sulphuric acid, which may under circumstances be cooled (German Patent 292,385; Norwegian Patents 28,762 and 31,438; French Patent 465,504). In German Patents 278,867 and 305,915 a mixture of nitric acid vapour and steam is carried into a scrubbing tower at 120° C.; this is charged above with 80 per cent. sulphuric acid at 30° C. in such quantity that the temperature of the escaping

[1] *Zeitsch. f. angew. Chem.*, 1918, i., 48.
[2] *Chem. Zentralbl.*, 1919, iv., 72, 177; *Zeitsch. f. angew. Chem.*, 1917, i., 238.

gases is about 95° C. According to German Patent 318,091, dilute nitrous gases are absorbed by sulphuric acid of about 90 per cent. strength. Nitrosyl sulphuric acid is thus formed—

$$2SO_2\begin{cases}OH\\OH\end{cases} + N_2O_3 \rightleftharpoons 2SO_2\begin{cases}OH\\ONO\end{cases} + H_2O$$

which, when at this concentration, can be readily freed from its nitric oxides by heating. According to German Patent 319,115, the heat of the nitrous reaction gases from the furnace, at a temperature of 1,000° C., is used for concentration purposes. According to German Patent 323,961, the hot acid vapours and steam from the concentrating plant are cooled and condensed with the help of a gas current previously passed through a refrigerating liquid.

H. Pauling's German Patent 299,774 deals with an apparatus and rectifying column for the concentration of sulphuric acid. A nitric acid concentration process is described in German Patent 305,553. The arrangement is illustrated in Fig. 72. The nitric acid to be concentrated and the sulphuric acid used as a dehydrating agent are heated either separately or in admixture. The hot mixture is then passed in counter current to air or some other inert gas. The dilute nitric acid is passed through the steam - jacketed container, a, and the concentrated sulphuric acid through b. Both acids enter at the top of the column c, which contains any suitable filling, at 90° to 95° C. This column contains at the top an arrangement for mixing the acids. An air current passes into

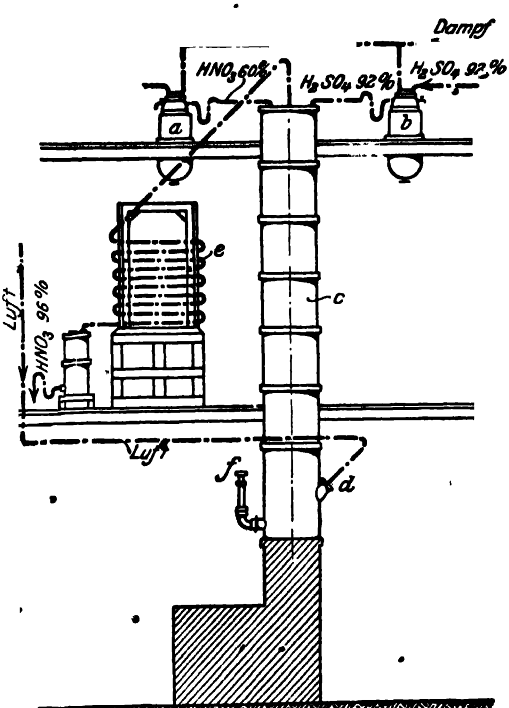

FIG. 72.

Dampf = Steam. Luft = Air.

the column below, through *d*, and expels the nitric acid from the mixture. The air laden with nitric acid vapours leaves the column above and enters the condenser, *e*, in which the nitric acid vapours are condensed, whilst air free from nitric acid escapes. Sulphuric acid free from nitric acid is discharged from the column at *f*, and is separately concentrated.

The addition of strong sulphuric acid to aqueous nitric acid lowers the vapour pressure of the water in the latter to such an extent that almost pure nitric acid evaporates on heating.[1] The Pauling process is now used very widely, the initial constructional difficulties having been overcome. According to F. Foerster, Th. Burchardt and E. Fricke[2]: "It has been developed into a very simple and elegant method of converting nitric acid of about 50 per cent. concentration, as obtained from the nitrous gases from ammonia oxidation into highly concentrated acid of 96 to 98 per cent." R. Reik[3] also publishes a very favourable opinion on the process which survived the test of practical application during the War.

In German Patent 297,901 Farbenfabriken vorm. Fr. Bayer & Co. describe apparatus and a process by which a mixture of dilute nitric acid and concentrated sulphuric acid is fractionated by the heat of nitric acid vapours. According to German Patent 297,903, 600 kg. of steam and 5,000 cu. m. of air are gradually injected into 10,000 kg. of a mixture containing 50 per cent. of H_2SO_4 and 20 per cent. of HNO_3 in a container of 10 cu. m. capacity; simultaneously 2,500 kg. of 80 per cent. sulphuric acid are run in through an attached drying tower. In this manner 2,050 kg. of pure nitric acid of 96 per cent. concentration are obtained, leaving 11,000 kg. of 68 per cent. sulphuric acid almost free from nitric acid. When a concentration column is charged with nitric and sulphuric acids, the sulphuric acid is employed at such a temperature and concentration, and nitric acid of 40 to 50 per cent. concentration is added in such quantity, that sulphuric acid of 74 per cent. concentration is discharged from the bottom of the column at 100° C. (German Patent 310,081).

In connection with the method of Farbwerke vorm. Meister Lucius & Brüning, Höchst-a.-M. already referred to (German Patent 296,809), we may mention the similar U.S. Patent 1,180,061 of M. Moest and the Nitrum A.G., Zürich. F. Raschig concentrates mixed nitric and sulphuric acids in a system of evaporating pans (German Patent 286,973). According to C. Hofmann and H. Josephy (German Patent 292,543) a mixture of meta- and pyrophosphoric acids exerts

[1] See Jul. Baumann, *Chem. Ztg.*, 1920, p. 805.
[2] *Zeitsch. f. angew. Chem.*, 1920, i., 132.
[3] *Österr. Chem. Ztg.*, 1919, p. 140.

a powerful dehydrating action, and is obtained on evaporating aqueous solutions of phosphoric acid at 220 to 330° C. If 25 volumes of 49 per cent. nitric acid are heated with 50 volumes of such phosphoric acid, nitric acid of 95 to 98 per cent. concentration and specific gravity 1·51 distils between 105° and 120° C. The Deutsche Gasglühlicht A.G. (Auer-Gesellschaft) fractionates nitric acid of less than 69 per cent. concentration with dilute sulphuric acid of about 78 per cent. concentration (German Patent 299,681). Other methods of concentrating nitric acid are described in German Patent 300,712 of Wülfing, Dahl & Co., and German Patent 302,534 of H. Petersen. A. Clemm (German Patents 303,313 and 304,233) concentrates nitric acid by decomposing barium nitrate with sulphuric acid. E. Reinau treats dilute nitric acid with sodium sulphate (German Patents 299,001 and 299,007) and relies on the reactions :—

$$HNO_3 + xH_2O + Na_2SO_4 = NaNO_3 + NaHSO_4 + xH_2O$$
$$\text{and } NaNO_3 + NaHSO_4 = HNO_3 + Na_2SO_4.$$

Concentrated nitric acid may be distilled from a solid mixture of nitrate and bisulphate (German Patent 305,171).

The "Techn. Büro für chem. Industrie, 'Agd' G.m.b.H. vorm. Ing. Düron," Wiesbaden, constructs nitric acid concentration plants, for example, according to German Patent 309,153, constructed of Agdiron metal, which is extremely resistant to acids. An interesting controversy ensued from the publication of K. Mattenklodt on the Strzoda concentration system for sulphuric or nitric acid (German Patent 272,158), which was found to be satisfactory in practice.[1] (See also German Patent 323,416 by C. F. Baer.)

Supplement, 1921–24

Articles of General Character on Absorption.—L. Maugé, *In. Chim.*, **7**, 265 ; Pascal, *loc. cit.*, p. 227 ; Pauling, *Zeitsch. f. angew. Chem.*, **36**, 71 (1923) ; *J. Soc. Chem. Ind.*, **39**, 236 (1920) ; **41**, 285 (1922).

The exceedingly important theory of the condensation process is dealt with by Burdick, Freed, Clement, Pinkus, Schulthess, Sanfourche, Webb, Bodenstein, Lueck, Briner, Pollak, Berl, and others, in *Journ. Amer. Chem. Soc.*, **43**, 518 (1921) ; **43**, 292 ; **44**, 757 ; *Zeitsch. f. Elektrochem.*, **27**, 110 (1921) ; *Helv. Chim. Acta*, **1**, 141 (1919) ; **5**, 432 (1922) ; *Compt. rend.*, **169**, 1397 (1920) ; **172**, 1573 (1921) ; *Journ. Soc. Chem. Ind.*, **40**, 7, 162 (1921) ; *Zeitsch. phys. Chem.*, **100**, 68, (1922) ; **101**, 150 (1922) ; *Journ. de Chim. phys.*, **19**,

[1] *Chem. Ztg.*, 1920, pp. 529, 683 ; 1921, p. 20.

290 (1921); *Zeitsch. f. angew. Chem.*, **1923**, 87; *Zeitsch. anorg. Chem.*, **1923**, 179.

The most important feature of the patent literature is the intermediate production of unstable compounds, already referred to, during the treatment of the nitrous gases, in order to enable these to be concentrated (Norsk Hydro, l'Azote Français, and others): German Patents 325,637, 329,179, 336,944, 340,988, 298,846, 304,372, 331,591, 345,668, 359,567; Norwegian Patents 28,767, 32,905, 33,078; French Patents 525,572, 521,731, 520,963, 532,794; U.S. Patents 1,407,530, 1,427,441.

Concentration of Dilute Nitric Acid.—Articles of general interest are contained in *Chim. et Ind.*, **3**, 576 (1920); *Zeitsch. f. angew. Chem.*, **34**, 164 (1921); *Rev. de Chim. Ind.*, **29**, 38; **30**, 215 (1921); **31**, 126 (1922); *Journ. Soc. Chem. Ind.*, **41**, 246; *Chem. Ztg.*, **1922**, 38; *Zeitsch. f. angew. Chem.*, **35**, 201, 206; **35**, 117; **36**, 87, 533, 565; *Ann. de Chim.* (9), **15**, 253; *Chem. Met. Eng.*, **26**, 443 (1922). German Patents 323,961, 329,179, 336,011, 336,811, 225,706, 340,360, 302,411, 335,762, 335,910, 272,158, 330,019, 303,271, 307,613, 340,905, 343,146, 303,391, 306,412, 307,944; Norwegian Patents 31,438, 28,762, 32,905, 32,489; Swiss Patents 87,963, 89,047; French Patents 519,530, 535,433; British Patents 170,840/1921, 164,734/1921; Austrian Patents 84,774, 88,583, 87,472. Most of these deal with the use of sulphuric acid as a dehydrating agent. Those patents are of most interest which are concerned with the removal of nitrogen oxides by refrigeration. German Patents 325,636, 340,864; Swiss Patent 88,552.

The following patents are concerned with denitration processes: German Patents 299,680, 341,886/7, 323,416, 332,198, 303,892; Austrian Patents 88.343; *Journ. Soc. Chem. Ind.*, **1921**, **40**, 265; *Chem. Met. Eng.*, **26**, 642 (1922).

Plant for the nitric acid industry, constructional materials, etc., are dealt with in German Patents 306,001, 321,879, 322,236, 336,561, 346,187; *Chem. Ztg.*, **1921**, 495; **1922**, 128, 1019; *Metallbörse*, **1924**, 149, 173.

CHAPTER XXVII

The Salts of Ammonia and of the Nitrogen Oxy-Acids

We do not propose in what follows to offer a complete picture of this special branch of technology or to enumerate all the literature and patents which have so far appeared ; we merely wish to glance at the newest information on the question in so far as it is concerne with the treatment of the synthetic products primarily produced—namely, ammonia and nitric acid.

The manufacture of fertilisers constitutes the most important application of synthetic ammonia.[1] Of such fertilisers ammonium sulphate is to-day the most important.

The ammonia used for this purpose, apart from coke-oven ammonia, is either in the form of gas or of concentrated ammonia solution. The latter is distilled either alone or after addition of milk of lime and converted into pure ammonia gas by systematic cooling in condensers (German Patents 281,095, 299,621, 303,832, 312,933, 314,362, 316,594, 320,415, 321,600, 323,306, 324.582; and *Chem. Zentralbl.*, 1919, iv., 1121). The ammonia obtained from calcium cyanamide can be used directly if sufficiently pure, without being first converted into ammonia solution and redistilled. The gas supplied from the condensers contains a high percentage of ammonia, accompanied by comparatively small quantities of water vapour and air. It also contains all those impurities, often in traces only, which act so prejudicially as catalyst poisons if the gas is subsequently oxidised to nitric acid. It is very often desired to recover the gas in the form of a very pure concentrated solution of ammonia or of ammonium carbonate. Numerous proposals and processes for these purposes are to be found in the literature.[2] The effluents from the distillation of ammonia solution or gas liquor must be continuously controlled if they are not to be sources of loss. Many processes have been evolved for the treatment of these liquors (German Patents 286,971, 291,038, 307,652).[3]

According to H. L. Kropf,[4] of the Zuidergaswerk, gas liquor has the following composition :—

[1] See C. Bosch, *Zeitsch. f. Elektrochem.*, 24, 361 (1919).

[2] German Patents 297,311, 302,195 ; *Chem. Apparatur*, 4, 161 (1917) : *Journ. f. Gasbel.*, 1915, p. 115 ; *Chem. Zentralbl.*, 1919, ii., 908.

[3] *Journ. f. Gasbel.*, 1918, p. 200 ; *Chem. Ztg.*, 1919, *Chem. Techn. Übers*, p. 187 ; *Chem. Zentralbl.*, 1919, iv., 472.

[4] *Chem. Ztg.*, 1917, *Chem. Techn. Ubers*, p. 60.

Total ammonia, 16·39 gm. per litre.			Total sulphur, 2·91 gm. per litre.		
In the form of	Per litre.		Per litre.		Per cent.
$NH_4 \cdot SH$	3·84 gm.	=	1·28 gm. NH_3	=	7·81 of total NH_3
$(NH_4)_2CO_3$	36·48 ,,	=	12·92 ,,	=	78·83 ,,
NH_4Cl	7·03 ,,	=	2·05 ,,	=	12·51 ,,
NH_4CNS	0·53 ,,	=	0·12 ,,	=	0·73 ,,
$(NH_4)_2SO_4$	0·28 ,,	=	0·04 ,,	=	0·24 ,,
$(NH_4)_2S_2O_3$	0·49 ,,	=	0·11 ,,	=	0·67 ,,
$(NH_4)_2Fe(CN)_6$	0·14 ,,	=	0·02 ,,	=	0·12 ,,

In certain circumstances, gas liquor may corrode concrete tanks [1] and should never be stored in galvanised iron tanks.[2] According to German Patent 292,145, gas liquor may be converted directly into fertilisers.

H. Haakh heats potassium ferrocyanide with water in autoclaves to 200° C. and obtains ammonia and potassium formate (German Patent 281,044). E. P. Williams (British Patents 2,841/1914, 23,624/1909) heats calcium sulphocyanide in solution with an alkali or alkaline earth in presence of water. According to German Patents 313,271 and 316,757, urea is converted into ammonium salts by the addition of waste potash lye.

Pure ammonia gas may be used for various purposes including the preparation of alkali amides (German Patent 323,004) the neutralisation of fats and oils (German Patent 312,136), and as an addition to gas for filling balloons [3] (German Patent 303,966). It is quite generally used in refrigerating machines and as a liquefied gas for refrigeration purposes.[4]

The important question of the improvement of the yield of ammonia in the gasification of coal, peat,[5] coke, and so forth, cannot be considered here, being outside the field which we are discussing (see German Patents 281,096, 288,524, 298,861, 301,979, 303,954, 311,694, 312,426, 313,470).[6]

On the manufacture of ammonia sulphate we may refer more especially to the publications of J. Rodenburg, W. Bertelsmann, P. Smit and E. Wolff, dealing with manufacturing experiences, difficulties and control.[7] Leybold [8] discusses a case of poisoning by saturator gases and Jänecke [9] writes on the melting and boiling points

[1] *Chem. Ztg.*, 1917, pp. 161, 249; 1918, p. 195.
[2] *Journ. f. Gasbel.*, **60**, 63 (1917).
[3] *Chem. Ztg.*, 1915, p. 325.
[4] *Journ. f. Gasbel.*, 1917, p. 399; *Chem. Zentralbl.*, 1920, iv., 640, 644.
[5] E. Philippi, "Torfkraftwerke und Nebenproduktenanlagen" (Berlin, 1919).
[6] "Dissertations" of Sommer, Breslau and Sachs, Karlsruhe; *Zeitsch. f. angew. Chem.*, 1919, i., 148; *Feuerungstechnik*, **6**, 3–8 (1917).
[7] *Het Gas*, January, 1915; *Chem. Ztg.*, 1917, *Chem. Techn. Übers*, p. 252; *Journ. f. Gasbel.*, 1918, pp. 577, 601; *Chem. Weekblad*, **14**, 955 (1917).
[8] *Chem. Ztg.*, 1917, *Chem. Techn. Übers*, p. 224.
[9] *Zeitsch. f. angew. Chem.*, 1920, i., 278.

of ammonium sulphate. Much work has recently been devoted to the manufacture of an absolutely neutral product, especially in England.[1] Free sulphuric acid impairs the storing qualities of the product. According to Atwater and Schulze [2] it is best to dry the sulphate in a current of hot air. A salt containing less than 0·25 per cent. of water is alleged permanently to retain its spreading properties. The reason why certain qualities cake and become moist is considered by the authors to be a small admixture of pyridine sulphate. J. Poulson [3] writes on the work necessary for establishing an ammonium sulphate plant. The whole subject has been discussed in such detail in the chapters on Ammonia and on Ammonium Compounds written by Bertelsmann for Ullmann's "Encyclopædia," [4] and by F. Muhlert in "Die Industrie der Ammoniak und Cyanverbindungen" (Leipzig, 1915), that it will only be necessary here to offer a short survey of the latest literature,[5] especially as we have already discussed similar matters in connection with our description of the Haber-Bosch process.

Complete ammonium sulphate installations are described by Barnick, Borngräber, Reinhardt, and Heinecken.[6] L. Fabre [7] describes the manufacture of ammonium sulphate from gas liquor in gas works with the minimum amount of manual labour. A special type of saturator is used called the "Excelsior," and a special "Zenith" hydro-extractor. Details of saturator construction are described in German Patents 286,242, 288,497, 289,162, 289,524, 297,740, 310,124, 314,598, 316,595, and 322,601. German Patent 284,641 of Gebr. Hinselmann describes a process for the production of perfectly white ammonium salts from discoloured crude salts. In German Patent 205,715 F. Dahl describes a method of avoiding the formation of lumps in ammonium sulphate by the immediate addition of alkali chloride or sulphate. A.G. J. F. Collins, Dortmund, describes a special method of fishing ammonium sulphate from the saturator in German Patent 316,596. The manufacture of ammonium sulphate is also dealt with in British Patents 28,072/1912, 28,245/1913, and U.S. Patents 1,105,607 and 1,163,753. According to British Patent, 127,398/1918 neutral or even ammoniacal ammonium sulphate is obtained by washing the product initially obtained with a cold, saturated ammoniacal solution of ammonium sulphate.

We have already discussed patents dealing with the oxidation of

[1] *Chem. Zentralbl.*, 1919, iv., 601.
[2] *Chem. Ztg.*, 1920, *Chem. Techn. Übers*, p. 192.
[3] *Chem. News*, **120**, 8–9 (1920).
[4] Vol. i., p. 360 (1914).
[5] *Chem. Ztg.*, 1913, No. 110; 1915, Nos. 118, 119; 1920, p. 625.
[6] *Chem. Apparatur*, 1915, p. 61; 1918, p. 17; *Journ. f. Gasbel.*, 1915, p. 64; 1919, p. 30.
[7] *Rev. de Chim. Ind.*, **28**, 384 (1919).

ammonium sulphite to ammonium sulphate in connection with processes for the manufacture of nitrogen (see German Patents 283,161, 283,618, 302,671, 316,502). These processes are of great interest, as they enable the SO_2 of flue gases to be utilised under certain circumstances with production of ammonium sulphate and by-product nitrogen.

A mixture of ammonium sulphate and ammonium nitrate containing an average of 27 per cent. N was placed on the market by the Leuna Works under the name of Ammonsulfatsalpeter (ammonium sulpho-nitrate). The catastrophe at Oppau in September, 1921, was due to an explosion during the blasting of ammonium sulpho-nitrate. The following analyses are supplied by H. Ulex [1]:—

By Arnd's Method.	By Ulex's Method.
26·44 per cent. N.	26·90 per cent. N.
26·75 ,,	27·18 ,,
26·96 ,,	27·41 ,,
26·71 ,,	27·07 ,,

H. Hampel [2] points out the possibility of fixing ammonia with crude potassium salts. These methods, which resemble the well-known gypsum process of the B.A.S.F., are of considerable importance in Germany, as the domestic supply of sulphuric acid is very scanty, and pyrites from abroad has to be purchased at very high prices.[3] Jul. Baumann explains the circumstances with the help of exact statistics.[4]

During the War large quantities of sodium bisulphate (nitre cake) [5] were available in Germany, England, France, and other countries, as a by-product of the explosive industry. The suggestion was soon made that this should be used for the fixation of ammonia. Theoretically nitre cake should contain the equivalent of 40·8 per cent. of free sulphuric acid, whilst in practice it usually contains 30 to 35 per cent. only. It becomes difficult to use if the contents of nitric and nitrous acids, nitrates, and so forth, exceed 0·25 per cent., for the lead saturators are then seriously attacked. It is generally advisable not to use sodium bisulphate exclusively, as otherwise the salt which is produced contains too little nitrogen—8 to 10 per cent. of NH_3—but to mix it with sulphuric acid before using it for absorption.[6] Details of such processes are dealt with in German Patents 298,042 and 292,742. Norwegian Patents 31,040, 31,041 and 31,042

[1] *Chem. Ztg.*, 1920, p. 876; see also *Chem. Zentralbl.*, 1920, iv., 570.
[2] *Chem. Ztg.*, 1919, p. 617; German Patent 321,030.
[3] *Zeitsch. f. angew. Chem.*, 1919, ii., 796.
[4] *Chem. Ztg.*, 1920, p. 346.
[5] See German Patent 322,601; $Na_2CO_3 + (NH_4)_2SO_4$ from bisulphate.
[6] *Journ. f. Gasbel.*, 1918, p. 91; *Chem. Ztg.*, 1919, p. 500, and *Chem. Techn. Übers*, p. 313; *Chem. Zentralbl.*, 1919, ii., 559; iv., 219, 536.

describe a method of separating mixtures of sodium and ammonium sulphates into Glauber salt and ammonium sulphate by suitable addition of water.[1] By boiling with suitable quantities of water, the anhydrous components may also be separated. If the salt

$$Na_2SO_4 + (NH_4)_2SO_4 + 4H_2O$$

is heated with a solution of ammonium sulphate, sodium sulphate separates first, whilst ammonium sulphate only separates on cooling the mother liquor. If the double salt is heated to 350° to 600° C., all the ammonia is driven off as a volatile gas, and sodium bisulphate remains. J. Mościcki and W. Dominik [2] have shown that the whole of the sulphuric acid may be distilled from the bisulphate after mixing it with an equal quantity of sand or of sulphate. On the basis of their experiments an installation was erected in Vienna. The use of nitre cake has practically ceased to be of any importance in Germany, and in consequence of the decline in the explosive industry only very small quantities are marketed.

We have already discussed the gypsum-ammonium sulphate process of the B.A.S.F. and its application to Haber ammonia, and it will therefore suffice here to mention German Patents 299,621 and 291,622 of Dr. C. Otto & Co., Dahlhausen-a.-R., which deal with a reaction column for the interaction of ammonium carbonate, gypsum, and so forth. The Chem. Industrie A.G. and Fr. Wolf (Bochum) deal with the production of ammonium sulphate from gas liquor, gypsum and carbon dioxide under pressure in German Patent 299,752. We may here call attention to the attempts which have been made to utilise the sulphur contents of coal for the fixation of the ammonia, that is, by utilising the sulphur in spent oxide for the purpose.[3] The essential patents dealing with this question are : German Patents 290,509, 300,035, 300,036, 300,383, 301,464, 302,562, 306,441, 307,081, 309,159, 314,598, 314,627, 314,628, 318,671, 325,652, 325,966 ; French Patents 476,463, 480,129 and British Patent 17,475/1914.

The manufacture of ammonium nitrate is described by Bertelsmann ; [4] as carried out commercially to-day it may be divided into two groups of processes :—

(1) The neutralisation of nitric acid in solution with a solution of ammonia, and

[1] *Journ. f Gasbel.*, 1919, p. 97.
[2] *Chem. Zentralbl.*, 1920, iv., 430.
[3] *Journ. f. Gasbel.*, 1918, p. 152, 161 ; 1919, pp. 3, 77 ; *Chem. Ztg.*, 1917, p. 657 ; *Chem. Techn. Übers*, 1919, pp. 250, 299 ; 1920, p. 742 ; *Chem. Zentralbl.*, 1919, iv., 269, 270, 298, 385 ; 1920, ii., 462, 463, 464 ; iv., 707 ; *Zeitsch. f. angew. Chem.*, 1920, i., 141 ; *J. Soc. Chem. Ind.*, **36**, 483 (1917).
[4] *Loc. cit.*

(2) Neutralisation of nitric acid in solution by gaseous ammonia.

In both cases the acid and ammonia are mixed in accurately regulated proportions in water-cooled vessels of stoneware, enamelled cast-iron, or wrought iron with an acid-proof lining. The solutions so obtained are purified, filtered and then evaporated. They are either concentrated to such a point that the liquors which are drawn off set in the crystallisers to a paste, which is then treated in a centrifuge, or the whole of the water is driven off in enamelled cast-iron vacuum pans provided with stirrers, and the whole contents of the pans, which are perfectly pure, are then discharged into conveyors. Latterly a concentrated solution from the vacuum pans has been dried completely on vacuum drums provided with scrapers. Quite recently methods have been introduced in which the concentrated solution is evaporated as a spray.

The ammonium nitrate works at Notodden has been described in detail with an accompanying plan by F. A. Bühler, of Berlin (now W. Salge & Co., G.m.b.H.[1]) its erector. Bühler makes use of rocking crystallisers [2] and rapid driers of special construction, and has constructed similar plants for the Sprengstoff A.G. Carbonit, of Hamburg. At the Exhibition of Scientific Products at the Central Hall, Westminster, in August, 1919, Brunner, Mond & Co., Ltd., showed needle-shaped crystals of ammonium nitrate about 2 ft. long, and also ammonium chloride briquettes with the trade name "Salamac," which resembled in size and appearance a pound bar of soap. Ammonium nitrate has also been briquetted and converted into tablets. In the *Chem. Ztg.*, 1916, p. 1049, C. Gautsch published tables dealing with the manufacture of ammonium nitrate solutions of all the usual strengths.

In German Patent 299,602 the Bamag describe a process by which the amount of water to be evaporated when neutralising dilute nitric acid with gaseous ammonia is reduced to a minimum. German Patent 325,074 of J. R. Partington and G. J. Jones describes the direct separation of finely divided solid ammonium nitrate. According to German Patent 302,034 the Norsk Hydro convert dilute nitrous gases into ammonium nitrate, which is converted into granular form according to their German Patent 304,912. According to German Patent 304,087 ammonium nitrate is rendered less hygroscopic by adding sufficient quantities of gelatine, albumin, dextrine, and so forth, to the solution. According to German Patent 309,668 of the B.A.S.F., comparatively non-hygroscopic bodies for fertilisers are obtained from ammonium nitrate and potassium

[1] *Chem. Ind.*, 1911, p. 210.
[2] See also *Chem. Zentralbl.*, 1919, iv., 534.

chloride known as "potash ammonium nitrate" containing on the average 16 per cent. of N and 25 to 27 per cent. of K_2O. In German Patents 305,556, 305,557, 305,558, 321,878, the Dynamit A.G. vorm. Alfr. Nobel & Co., Hamburg, melt ammonium nitrate with the addition of dicyandiamide as a flux, and cast it in moulds. The following patents should also be noted:[1] U.S. Patents 1,126,471, 1,131,361, 1,217,247; British Patent 1,820/1914.

German Patents 271,518 and 294,991, British Patent 26,233/1913, and French Patent 465,683 deal with the double decomposition of solutions of ammonium salts with alkali nitrates, more particularly with the interaction of ammonium sulphate and sodium nitrate. O. Matter manufactures alkali azides from alkali amides and nitrous oxide according to German Patents 302,561 and 310,090.

The manufacture of ammonium nitrate explosives is described, for example, in German Patents 302,460, 303,370, 303,929, 303,979, 307,040, 317,030; French Patents 477,776 and 477,777; and U.S. Patents 1,343,063 and 1,343,077.[2]

After numerous experiments had shown that ammonium chloride could quite well replace ammonium sulphate as a fertiliser,[3] more attention has been turned to the manufacture of the latter. We have already mentioned that the B.A.S.F. use a modified ammonia soda process for the manufacture of ammonium chloride. We must here refer more particularly to German Patents 271,421, 286,183, 292,304 and 306,359, and to articles [4] by H. Barnick and W. Strommenger. A. Riedel recovers ammonium chloride from blast-furnace gases according to German Patent 319,550.

Special interest has been aroused by the proposals of M. Gerlach on the manufacture of so-called ammonium phosphates from superphosphates and ammonia according to German Patent 282,915 [5] (see also German Patents 292,530, 307,093 and 314,404). In the United States the Ammo-Phos Corporation manufactures ammonium phosphate on a large scale; it passes ammonia into a phosphoric acid solution obtained from crude mineral phosphate and sulphuric acid and evaporates *in vacuo*;[6] see U.S. Patents 1,100,638, 1,103,115, 1,112,183, 1,115,044, 1,142,068, 1,145,107, 1 146,222, 1,167,788, 1,208,887; British Patent 25,365/1913).

The manufacture of ammonium carbonate of uniform quality,

[1] *Chem. News*, **116**, 175 (1917).

[2] See also German Patent 307,107; *Chem. Zentralbl.*, 1919, ii., 452, 700; iv. 514, 696; *Chem. Ztg.*, 1916, "Repertorium," p. 3; *Chem. Ztg.*, 1919, *Chem. Techn. Übers*, pp. 198, 230.

[3] *Ernährung der Pflanze*, 1916, p. 89; *Chem. Ind.*, 1918, Nos. 11, 12.

[4] *Chem. Apparatur*, 1915, p. 33; *Montan. Rundschau*, 1915, p. 68; *Kali*, 1916, p. 55.

[5] *Zeitsch. f. angew. Chem.*, 1916, i., 13, 18, 200, 246; 1918, i., 91.

[6] *Chem. Ztg.*, 1918, p. 50.

which is difficult on account of the volatility of the components and the instability of the final product,[1] is described in German Patents 237,524, 246,017, 252,276, 285,498, 285,531, 286,241, 289,300, and 318,827. Ammonium carbonate has also been recommended as a fertiliser.

Among more general patents dealing with the manufacture of ammonium salts,[2] we may mention German Patents 290,756, 314,234, 319,550, French Patent 468,535, and British Patent 29,047/1913.

We have frequently dealt with the technology of nitrates in the previous chapters so that it is only necessary here to mention certain further details. The double compounds, potassium ammonium nitrate and sodium ammonium nitrate,[3] are of special interest, as are the attempts to manufacture potassium nitrate, this being a particularly valuable fertiliser.[4] Calcium nitrate obtained by the arc process [5] can with advantage be further treated in order to improve its properties (U.S. Patents 1,122,923, 1,143,625; British Patent 5,184/1914). There are a number of patents by E. Reinau on the manufacture of alkali nitrates from nitric acid, water and alkali sulphates (German Patents 299,001, 299,002, 299,003, 299,004, 299,005, 299,006, 299,007, 300,697, 301,703, 305,062, 324,379).

Sodium nitrite is manufactured from the nitrate by melting the latter with lead,[6] but it may be manufactured directly from nitrous furnace gases by suitable means (see German Patent 188,188, already referred to). The electric reduction of nitrates (Norsk Hydro, German Patent 321,771) often leads to the production of free alkali and ammonia.[7]

Supplement, 1921–24

AMMONIUM SULPHATE.—*By Oxidation of Ammonium Sulphite and Ammonium Sulphide.*—German Patent 342,623; Norwegian Patent 30,822; *Ber.*, 2425 (1922).

By Absorption with $NaHSO_4$ and Decomposition of the Sodium Ammonium Sulphate.—German Patents 322,601, 345,865, 351,217, 336,560, 337,217; Swiss Patent 93,737; U.S. Patents 1,364,822, 1,366,301, 1,366,303; French Patent 497,465.

[1] *Chem. Ztg.*, 1920, p. 347; 1915, p. 878.

[2] *Zeitsch. f. angew. Chem.*, 1916, i., 339; 1920, ii., 379.

[3] *Deutsche Zuckerind.*, 1918, **43**, 119; *Ill. Landw. Ztg.*, **38**, 412.

[4] *Österr. Chem. Ztg.*, 1918, p. 7: *Chem. Zentralbl.*, 1919, iv., 78; *Chem. Techn. Wochenschr.*, **2**, 121 (1918).

[5] *J. Soc. Chem. Ind.*, **36**, 771 (1917).

[6] *Ibid.*, **34**, 585.

[7] Articles of general interest are: *Chem. Ztg.*, 1917, pp. 732, 788; 1919, p. 295; *Zeitsch. f. angew. Chem.*, 1918, ii., 435; *Zeitsch. kompr. flüss Gase*, **19**, 37; **20**, 17; *Chem. Ind.*, 1919, p. 330; *Apothek.-Ztg.*, 1919, p. 167; *Journ. f. Gasbel.*, 1918, p. 536; *Chem. Zentralbl.*, 1919, ii., 54, 558; iv., 7, 219, 404, 534, 601, 1101; 1920, ii., 72; iv., 119, 279; *Österr. Chem. Ztg.*, 1917 (2), 76; *Chem. Eng.;* 1910, 201; *Chem. News*, 1915, p. 167; *Met. Chem.*, 1917, p. 525.

Types of Saturators.—German Patents 328,394, 334,976, 335,305, 339,342, 345,255, 349,330, 353,370; British Patents 145,781/1920, 173,818/1922, 179,723/1920, 175,649/1922, 166,036/1921.

Purification, Decolorisation and Neutralisation of Crude Ammonium Sulphate.—British Patents 152,766/1919, 170,613/1920, 177,726/1921, 182,134/1922, 183,089/1921, 181,884/1921, 182,654/1922, 163,162/1920, 194,625/1922; U.S. Patents 1,360,785, 1,414,441, 1,412,549; French Patents 530,876, 524,902; German Patents 329,356, 332,116, 353,744, 340,595; *Chem. Met. Eng.*, **22**, 373 (1920); *Chem. Trade Journal*, **70**, 259 (1922); *Gas World*, **74**, 259; **75**, 243; **75**, 283 (1921); **76**, 1, 4, 28 (1922); *Engin.*, **112**, 135; *Wasser u. Gas*, **1921**, **11**, 553.

Ammonium Nitrate.—*Preparation.*—German Patents 326,930, 358,123, 347,369, 349,266; Dutch Patents 6,410, 6,649; *Pharm. Weekblad*, **57**, 1481; *J. Chem. Soc.*, **115**, 1387; **121**, 959, 963; *Compt. rend.*, **174**, 1466; **172**, 345.

Mixed Fertilisers.—Norwegian Patents 31,516, 33,787; German Patents 343,928, 332,115, 309,288; U.S. Patent, 1,406,455; *Chem. Ztg.*, **1920**, 876; **1921**, 20; *Compt. rend.*, **172**, 218, 345; **171**, 977.

General.—German Patents 334,189, 303,880, 307,010; *Gazz. Chim. Ital.*, **50**, ii., 81 (1920).

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ALKALI NITRITES.—German Patent 345,050; Swiss Patent 92,110; *Chem. Ztg.*, **1921**, 581, 796.

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CHAPTER XXVIII

Conclusion

THE contents of the preceding chapters illustrate and describe the extraordinarily important part which nitrogen plays in the economy of Nature and of mankind. After the chemistry of nitrogen and its many varying compounds had been studied in such detail for a long period—157 inorganic nitrogen compounds being known [1] —the news that Rutherford had been able to demonstrate the non-elementary nature of nitrogen in 1919 was all the more surprising.[2]

In 1920 the German nitrogen industry was in a very difficult position, which had attracted much public attention. There was a dearth of nitrogen for agricultural purposes, whilst the works had difficulty in disposing of their products, though these difficulties became somewhat less in the spring of 1921; the reason for this state of affairs was that the prices of the manufactured fertilisers were too high for the farmers. The Economic Commission of the Reichstag [3] allowed 25,000 tons of nitrogen fertilisers to be exported, and 30,000 tons later, in order that the internal price might be reduced from the profits so obtained. In 1920 the Prussian Minister of Agriculture, Braun, published a memorandum in which it was proposed to convert the nitrogen works into a Government monopoly, or at any rate to place the sale of fertilisers in the hands of the German Government, and to credit the agriculturalists with two-thirds of the purchase price, under certain guarantees. In pursuit of this idea the Minister demanded, at a meeting of the Main Committee of the Prussian Parliament in November, 1920, that 1,500,000,000 marks should be granted by the German Government to reduce the price of fertilisers, pointing out that by spending this sum, imports of food to the amount of 12,000,000,000 marks could be avoided. All these problems, closely connected with the general problem of the food supply of the German nation,[4] were discussed in detail in the middle of November, 1920, by the sub-committee for Agriculture and Food Supplies of the Temporary Imperial Economic Council; at this sitting J. Bueb and N. Caro gave expert evidence. Statements

[1] *Zeitsch. f. angew. Chem.*, 1919, i., 292.

[2] *Chem. Ztg*, 1919, pp. 556, 641; 1920, pp. 294, 301; *Zeitsch. f. angew. Chem.*, 1919, ii., 556; ii., 50, 124; *Umschau*, 20, 301.

[3] *Metallbörse*, 1920, p. 1359.

[4] *Zeitsch. f. angew. Chem.*, 1920, i., 31?.

regarding the Nitrogen Compensation Fund and the use made of sums derived from that source were publicly made at times, with considerable heat, as is evident, for example, from the protest [1] at the shareholders' meeting of the Mitteldeutschen Stickstoffwerke A.G., Piesteritz, on November 12th and 13th, 1920. At a meeting of the National Economic Council on December 13th, 1920, Ministerialdirektor Hoffmann stated that public money would not be expended in order to lower the price of fertilisers. We have already discussed these matters in greater detail in the Economic Section. The nitrogen industry is an unsuitable field for attempts at socialisation.

After great stimulation by the War and by the co-operation of all civilised countries, the nitrogen industry now presents a solid front. It will be the problem of the next few years further to develop certain of its processes. Some of the important questions to be solved are the perfection of methods of nitrogenating carbide, dust removal, the conversion of calcium cyanamide into more valuable nitrogen compounds, the study of the purely chemical production of calcium carbide by utilising the oxygen produced as a by-product in the liquefaction of air, and finally the cheap conversion of the acetylene obtained from carbide into other organic substances. At the Baltic Engineering Congress at Malmö, on July 13th to 18th, 1914, O. B. Carlson [2] of Mansbo, dealt at length with the utilisation of calcium cyanamide as a raw material of chemical industry. His interesting views, which have been emphasised by the newest work on the manufacture of cyanide by Bucher and Thorsell, have unfortunately received little general attention.

The German coking industry will necessarily direct its endeavours primarily to increasing the size of the ovens and to the fullest possible further use of mechanical devices. Insufficient attention is still paid to the gasification and coking of poorer fuels, more particularly of peat.

The liquid air industry should pay more attention than hitherto to the manufacture of argon as a by-product, and the application of by-product oxygen. The increasing production of nitrogen from flue gases is a very welcome development from the economic standpoint.

Attempts will be made during the next few years either to replace ammonium sulphate as a fertiliser by more suitable materials, or to avoid the separate addition of sulphuric acid in its manufacture from coal gas by utilising the sulphur contents of the gas itself. The fact

[1] *Magdeb. Ztg.*, No. 682, November 14th, 1920.
[2] *Zeitsch. f. angew. Chem.*, 1914, *Wirtschaftl. Teil*, p. 725.

is hardly recognised to-day that these gases often present a fairly copious source of ethylene and therefore of alcohol, although there are urgent economic reasons for the development of such manufacture.

Mixed fertilisers containing several fertilising elements in one compound have not yet received as much attention as they really deserve. The reason for this has already been pointed out. The increasing propaganda by the works will gradually help to remedy this state of affairs. In Germany the Badische Anilin und Sodafabrik, which is necessarily concerned with the fixation of the enormous quantity of ammonia which it produces, is the natural leader in this field. By the synthetic production of urea, which is quantitatively absorbed by the vegetable organism, and of ammonium carbonate, synthetic manufacture has turned full circle and now produces the essential ingredients of stable manure, which was used by our earliest ancestors to increase the yields of their holdings.

The part which may be played by ozone in the absorption of dilute nitrous gases and the results of the newest investigation in this field should not be neglected by the industry.

Even in Germany the leaching of ores and other raw materials by nitric acid might become of importance if this acid could be produced at a sufficiently cheap rate. If attempts to increase the nitric oxide yield from internal combustion engines meet with success, this process will have a very hopeful future.

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SUMMARY OF THE MOST IMPORTANT PERIODICAL LITERATURE FROM 1914 TO SPRING, 1921

CHAPTER I.—THE HISTORICAL DEVELOPMENT OF THE NITROGEN INDUSTRY BEFORE THE ADVENT OF ATMOSPHERIC NITROGEN FIXATION

Chem.-Ztg. **1913**, Nr. 110ff. ; **1915**, Nr. 118ff. ; **1919**, Nr. 43ff., 59ff., 131ff. ; **1920**, Nr. 102ff., chem.-techn. Ubers. S. 278 ; **1921**, S. 3ff., 152.
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CHAPTER II.—THE CHILEAN NITRATE INDUSTRY

Dei Technik in der Landwirtschaft **1920**, I, Nr. 5, S. 260ff.
Chem.-Ztg. **1915**, S. 129, 139, 148, 195, 207, 270, 323, 339, 394, 417, 439, 479, 503, 552, 560, 595, 620, 759, 777, 812, 892, 942, 1185 ; Repert. S. 159, 376, 387 ; **1916**, S. 88, 131, 154, 232, 271, 282, 323, 344, 431, 566, 614, 662, 698, 765, 826, 850, 912, 942, 953, 976, 994, 1016, 1026, 1038, 1066, 1080, 1099 ; **1921**, S. 251.
953, 976, 994, 1016, 1026, 1038, 1066, 1080, 1099 ; **1917**, S. 18, 48, 58, 71, 100, 101, 126, 206, 244, 270, 283, 352, 417, 444, 471, 480, 516, 526, 547, 556, 654, 828, 832, 875 ; **1918**, S. 16, 59, 108, 143, 191, 232, 275, 323, 364, 412, 418, 432, 460, 603 ; **1919**, S. 12, 60, 136, 151, 248, 304, 320, 372, 431, 432, 503, 516, 591, 652, 660, 671, 696, 716, 716, 775, 840, 896 ; **1920**, S. 8, 92, 135, 156, 172, 212, 236, 264, 352, 411, 491, 547, 632, 720, 856, 939 ; chem.-techn. Übers. S. 125 ; **1921**, S. 128.
Zeitschr. f. angew. Chem. **1918**, III, 74, 81, 92, 108, 164, 171, 290, 295, 350, 384, 390, 410, 434, 452, 470, 496, 499, 508, 590, 595, 622 ; II, 25 ; **1919**, II, 35, 54, 60, 63, 74, 79, 92, 192, 197, 295, 303, 350, 353, 429, 480, 496, 541, 569, 590, 593, 699, 743, 779, 815 ; **1920**, II, 19, 90, 114, 127, 145, 215, 234, 235, 238, 248, 260, 271, 286, 309, 405, 458, 467.
Ch. Ztrlbl. **1919**, II, 163, 542 ; IV, 1042 ; **1920**, IV, 36, 316.
Umschau **1920**, S. 332.
Metallbörse **1920**, S. 795, 798, 921, 1119, 1120, 1131, 1159, 1761, 2107.
Chem. Ind. **1919**, S. 191 ; **1921**, S. 76/77.
Chem. Met. Eng. **1920**, S. 339.
See also Supplement, p. 20.

CHAPTER III.—THE DEVELOPMENT OF THE ATMOSPHERIC NITROGEN INDUSTRY IN GERMANY AND ITS ECONOMIC FOUNDATIONS

(a) General

Chem.-Ztg. **1915**, S. 655 ; **1916**, S. 33, 269, 971, 1043, 1053 ; **1917**, S. 21ff., 376, 405, 440, 583 ; **1919**, S. 275, 689, 734, 799, 806, 827, 873, 896 ; **1920**, S. 396 ; chem.-techn. Übers. S. 22 ; **1921**, S. 251, 552, 765, 1012.
Zeitschr. f. angew. Chem. **1918**, I, 110 ; III, 320 ; **1919**, I, 325 ; II, 403, 437, 727, 749, 757, 765 ; **1920**, II, 90, 149.
Zeitschr. f. techn. Fortschr. **1916**, S. 33ff.
Deutsche Zuckerind. **1918**, S. 60.
Zeitschr. Ver. deutsch. Ing. **1919**, S. 235, 258, 877.
Umschau **1919**, S. 321ff., 798.

296, 307, 344, 357, 384, 404, 596, 696, 735, 776, 864 ; **1921**, S. 11, 14, 20, 36, 127, 132, 138, 154, 156, 162, 212.
Zeitschr. f. angew. Chem. **1918**, III, 13, 41, 62, 198, 257, 262, 297, 353, 370, 407, 450, 485, 488, 538, 571, 589, 610, 613, 637, 640, 645 ; **1919**, II, 6, 124, 175, 203, 218, 227, 228, 266, 317, 319, 352, 383, 401, 440, 441, 455, 466, 488, 495, 510, 529, 536, 567, 619, 718, 721, 735, 754, 769, 779, 782, 807 ; **1920**, II, 4, 47, 103, 106, 131, 135, 190, 229, 243, 283, 294, 309, 319, 334/5, 378, 410, 411, 418.
Südd. Ind.-Blatt **1919**, S. 1307 ; **1920**, S. 1021, 1169 ; **1921**, S. 309.
Die Technik in der Landwirtschaft **1920**, S. 709, 798.
Metallb. **1920**, S. 1238, 1616, 1854 ; **1921**, S. 112, 399, 2142 usw.

(m) German Agriculture and Nitrogen Supply

Chem.-Ztg. **1913**, S. 1259 ; **1915**, S. 764 ; **1916**, S. 317, 385 ; **1919**, S. 132, 160, 248, 252, 376, 400, 449, 712 ; chem.-techn. Übers. S. 137 ; **1920**, S. 247.
Zeitschr. f. angew. Chem. **1918**, III, 218, 429, 653 ; **1919**, II, 158, 239, 360. 434, 515, 680 ; **1920**, II, 61, 62, 144, 192, 271, 272, 410.
Die Futter- und Düngemittelindustrie **1916**, S. 25.
Tonind.-Ztg. **1918**, S. 539.
Umschau **1919**, S. 157, 809 ; **1920**, S. 265.
Stahl und Eisen **1919**, S. 1497.
Mitt. d. Landw. Ges. **1919**, S. 427, 451, 467.
Technik in der Landwirtschaft **1920**, S. 404, 465, 486, 639.
Ch. Ztrlbl. **1919**, II, 750 ; **1920**, II, 776 ; IV, 37, 38.

(n) Power Production from Coal, Lignite, Water and Other Sources.

Chem.-Ztg. **1916**, S. 766 ; **1917**, S. 92, 330 ; **1918**, S. 255, 507 ; **1919**, Nr. 43ff., S. 7, 187, 270, 438, 676 ; chem.-techn. Übers. S. 243 ; **1920**, S. 229, 536, 774.
Zeitschr. f. angew. Chem. **1918**, III, 142, 341, 558, 575 ; **1919**, II, 111, 127 ; **1920**, II, 142, 257.
Wasser **1917**, S. 115ff.
Zeitschr. d. Ver. deutsch. Ing. **1918**, S. 838 ; **1919**, S. 1081.
Ch. Ztrlbl. **1919**, IV, 530 ; **1920**, IV, 316.
Südd. Ind.-Blatt **1919**, S. 217, 839, 953, 1183, 1532, 1779, 1781, 1791, 1991, 2192, 2197, 2203, 2838, 2955, 3063, 3065 ; **1920**, S. 15, 685, 857, 1127, 1341, 1384, 1484, 1579, 1804 ; **1921**, S. 7, 155, 431, 443.
Umschau **1919**, S. 46, 62, 334, 432, 755, 858 ; **1920**, S. 14, 194, 341, 593, 664.
Techn. Rundsch. **1920**, Nr. 19, S. 26.
Die Technik in der Landwirtschaft **1919**, S. 54, 125 ; **1920**, S. 372, 376, 444, 599, 687, 698, 714, 766.
Metallb. **1921**, S. 547.
See also Supplement, pp. 121-122.

CHAPTER IV.—THE NORWEGIAN NITROGEN INDUSTRY

Chem.-Ztg. **1914**, S. 110/111, 1109 ; **1915**, S. 78, 113, 222, 320, 523, 539, 584, 647/8, 683, 843, 881, 911, 943, 983 ; **1916**, S. 18, 131, 154, 379, 808, 825, 827, 852, 871, 950, 1027 ; **1917**, S. 250, 255, 301, 478, 513, 539, 568, 602, 654, 686, 703, 760, 868, 887, 889 ; **1918**, S. 9, 59, 72, 220, 239, 371, 468, 595 ; **1919**, S. 44, 139, 228, 271, 311, 492, 503, 520, 584, 716, 775, 784, 806, 868, 896 ; **1920**, S. 171, 344, 542, 648, 696, 735, 830.
Zeitschr. f. angew. Chem. **1918**, III, 166, 203, 211, 239, 283, 309, 337, 385, 391, 447, 471, 502, 557, 607, 619, 646 ; **1919**, II, 7, 110, 194, 203, 237, 267, 434, 497, 530, 625, 681, 786 ; **1920**, II, 10, 92, 116, 151, 295, 368.

Metallb. **1920**, S. 1158, 1280; **1921**, S. 113.
Ch. Ztrlbl. **1920**, II, 485; IV., 357.
Chem. and Met. Eng. **1920**, S. 1082.
Südd. Ind.-Blatt **1920**, S. 1937/8.
See also Supplement, pp. 134–135.

Chapter V.—The Swedish Nitrogen Industry

Chem.-Ztg. **1912**, S. 1176; **1913**, S. 787, 1118; **1915**, S. 128, 253, 394, 478, 523, 683, 759, 788, 820, 854/5; **1916**, S. 44, 131, 281, 393, 523, 615, 825, 912, 924, 984, 992; **1917**, S. 102, 114, 155, 213, 255, 417, 671, 686, 717, 784, 851, 887, 907; **1918**, S. 47, 73, 79, 120, 167, 191, 251, 364, 407, 419, 796; **1919**, S. 12, 243, 439, 487, 896; **1920**, S. 39, 47, 278, 296, 467, 491, 547, 607, 623, 708; **1921**, S. 552.
Zeitschr. f. angew. Chem. **1918**, III, 229, 234, 239, 263, 341, 367, 379, 409, 432, 459, 529, 569, 610, 635; **1919**, II, 92, 258, 314, 376, 592, 623, 635, 637, 681, 778; **1920**, II, 13, 37, 43, 92, 104, 106, 460.
Seifensieder-Ztg. **1917**, S. 823.
Umschau **1917**, S. 669.
Journ. f. Gasbel. **1918**, S. 205, 217.
Südd. Ind.-Blatt **1920**, S. 1491, 1575.
See also Supplement, p. 144.

Chapter VI.—The Swiss Nitrogen Industry

Chem.-Ztg. **1915**, S. 612, 686; **1916**, S. 745; **1917**, S. 72, 496, 536, 924; **1918**, S. 11, 196, 263, 359, 376, 395, 432, 591; **1919**, S. 169, 182, 438, 805, 876, 893, 911; **1920**, S. 100, 422; **1921**, S. 79, 204.
Zeitschr. f. angew. Chem. **1918**, III, 60, 82, 96, 196, 233, 260, 261, 263, 283, 345, 438, 469, 509, 553, 586/7, 592; **1919**, II, 425, 497, 561, 735, 823; **1920**, II, 144.
Journ. f. Gasbel. **1918**, S. 465; **1919**, S. 104.
Chem. Ind. **1918**, S. 1849/50.
Ch. Ztrlbl. **1919**, IV, 653.
Umschau **1919**, S. 815; **1920**, S. 215.
Die Technik in der Landwirtschaft **1919**, S. 217; **1920**, S. 366, 576.
Metallb. **1920**, S. 1210.
Südd. Ind.-Blatt **1920**, S. 1775.
Neue Zürcher Ztg., Exportbeilagen Nr. 4, 5, 6, 7, 8, 9, 10, 12, 13, 14, 17, 20, 21, 22, 31; Jahr **1919**. Land- und Forstwirtsch. Beilage Nr. 27.
See also Supplement, pp. 156 157.

Chapter VII.—The Nitrogen Industry in the Austrian Succession States (German-Austria, Hungary, Czechoslovakia, Jugoslavia, Poland)

Chem.-Ztg. **1915**, S. 328, 438; **1916**, S. 33, 113, 610, 627, 651, 658, 983, 1027; chem.-techn. Übers. S. 392, 414; **1917**, S. 506, 555, 556, 588, 688, 736, 767, 880; **1918**, S. 39, 40, 52, 120, 220, 362, 251, 311, 324, 352, 400, 419, 505, 507, 541; **1919**, S. 35, 187, 243, 290, 752, 760; chem.-techn. Übers. S. 159; **1920**, S. 143, 264, 296, 455, 467, 532, 583, 603, 811, 864; chem.-techn. Ubers. S. 279; **1921**, S. 235.
Zeitschr. f. angew. Chem. **1918**, III, 19, 97, 163, 180, 203, 295, 309, 323, 341, 357, 385, 432, 447, 582; **1919**, II, 90, 147, 345; **1920**, II, 26, 46, 86, 99, 100, 103, 136, 180, 236, 421.

Südd. Ind.-Blatt **1920**, S. 1339.
Metallb. **1920**, S. 725, 1156/7, 1251, 1395, 1615, 1711, 1722, 1900, 2105.
See also Supplement, pp. 166–167.

Chapter VIII.—The French Nitrogen Industry

Chem.-Ztg. **1915**, S. 788, 843; **1916**, S. 88, 938ff., 1053; **1917**, S. 436, 480, 639, 654, 838; Repert. S. 192; **1918**, S. 63, 119, 172, 180, 412, 453; **1919**, S. 139, 290, 384, 455, 516, 673, 679, 687, **716**, **723**, 727, 775, **868**; **1920**, S. 7, 39, 88, 152, 172, 176, 183, 236, 278, 296, 352, 423, 491, 564, 582, 648, 655/6, 804, 884, 900; **1921**, S. 48, 116, 468, 500.
Zeitschr. f. angew. Chem. **1918**, III, 88/89, 102, 117, 128, 225, 274, 282, 287, 358, 458, 596; **1919**, II, 15, 93, 197, 502, 561, 681, 728, 807; **1920**, 19, 82, 115, 119, 178, 192, 211, 227, 239, 271, 276, 283, 294, 318, 341, 466.
Umschau **1919**, S. 8/9; **1920**, S. 75, 211, 255, 655.
Hesse-Grossmann, Englands Handelskrieg und die chemische Industrie. Bd. III, S. 47 bis 74, 86.
Südd. Ind.-Blatt **1919**, S. 1532; **1920**, S. 1061, 1179, 1583.
Metallbörse **1920**, S. 1160, 1198, 1318, 1855; **1921**, S. 547.
Die Technik in der Landwirtschaft **1920**, S. 360.
Ch. Ztrlbl. **1920**, II, 431, 637.
Compt. rend. **169**, S. 1039.
Techn. Rundsch. (Berl. Tagebl.) **1917**, Nr. 9.
Neue Zürcher Ztg. **1919**, Exportbeilage Nr. 3 und 18.
See also Supplement, pp. 188–189.

Chapter IX.—The British Nitrogen Industry

Chem. Ind. **1912**, S. 294; **1915**, S. 331; **1918**, S. 1653; **1920**, S. 261; **1921**, S. 76, 85.
Chem.-Ztg. **1915**, S. 67, 128, 131, 147, 488, 683, 984; Repert. S. 310; **1916**, S. 139, 244, 405, 556, 763, 864; Repert. S. 211; **1917**, S. 101, 209, 235, 289, 292, 322, 400, 480, 539, 575, 639, 688, 703, 708, 719, 784, 791, 851, 888; **1918**, S. 1, 100, 135, 156, 184, 204, 208, 215, 220, 239, 304, 347, 376, 407, 455, 467, 472, 479, 555, 599, 606, 610; **1919**, S. 7, 36, 44, 92, 244, 248, 279, 299, 340, 372, 406/7, 448, 503, 516, 526/7, 583, 651, 712, 806, 896, 927; **1920**, S. 25, 39, 134, 143, 152, 171/2, 176, 183, 189, 211, 264, 284, 352, 364, 386, 404, 411, 423, 472, 484, 491, 511, 540, 547, 552, 568, 575, 648, 696, 804; **1921**, S. 188.
Zeitschr. f. angew. Chem. **1918**, II, 125; III, 88, 117, 118, 131, 152, 238, 265, 282, 287, 299, 333, 363, 430, 453, 464, 508, 586, 618, 622, 629; **1919**, II, 15, 106, 135, 206, 298, 392, 498, 538, 587, 599, 625, 651, 681, 697, 727, 771, 787, 791, 795/6, 801, 813/4; **1920**, II, 13, 19, 21, 24, 25, 28, 34, 44, 60, 61, 72/3, 80, 91, 111, 127, 157, 164, 169, 170, 175, 191, 237, 248, 301, 303, 320, 342, 370, 375.
Chem. Ztrlbl. **1919**, II, 908.
Zeitschr. d. Ver. deutsch. Ing. **1918**, S. 839.
Journ. f. Gasbel. **1918**, Bd. 60, S. 591; Bd. 61, S. 49, 210; **1919**, Bd. 62, S. 109.
Südd. Ind.-Blatt **1919**, S. 3067.
Die Technik in der Landwirtschaft **1920**, S. 715, 780.
Umschau **1920**, S. 153, 174.
Metallbörse **1920**, S. 879, 1159, 1160, 1198, 1331; **1921**, S. 353, 547
J. Soc. Chem. Ind. **1920** [39], 213.
Engineering **1920**, Bd. 110, S. 218.
Neue Zürcher Ztg. **1920** (bes. 15. Juli 1920).
See also Supplement, pp. 223–224.

CHAPTER X.—THE NITROGEN INDUSTRY IN THE REMAINING EUROPEAN COUNTRIES (BELGIUM, ITALY, SPAIN, DENMARK, ICELAND, NETHERLANDS, RUSSIA, FINLAND, LATVIA, LITHUANIA, ESTHONIA, BULGARIA; EUROPE AS A WHOLE)

Belgium

Chem.-Ztg. **1919**, S. 671; **1920**, S. 423, 540, 552, 648, 687; **1921**, 159.
Zeitschr. f. angew. Chem. **1919**, II, 696.

Italy

Chem.-Ztg. **1911**, S. 1185; **1914**, S. 865; **1915**, S. 533; **1916**, S. 335; **1917**, S. 343, 480, 507, 539, 760, 880; **1918**, S. 180; **1919**, S. 560, 686, 799; **1920**, S. 135, 143, 171, 588, 620; **1921**, S. 212.
Zeitschr. f. angew. Chem. **1918**, III, 273, 308, 370, 384, 417/8, 431, 616; **1919**, II, 7, 135, 175, 188, 821; **1920**, II, 12, 131, 216, 249, 379, 438, 467, 471.
Journ. f. Gasbel. **1916**, Bd. 59, S. 426.
Die Technik in der Landwirtschaft **1920**, S. 687, 698.
Ch. Ztrlbl. **1920**, IV, 79, 329.
Metallb. **1920**, S. 1210.

Spain

Chem.-Ztg. **1915**, S. 417, 438; **1918**, S. 172; **1920**, S. 24, 172, 547, 655.
Zeitschr. f. angew. Chem. **1918**, III, 83, 149, 305, 365; **1919**, II, 303, 312, 703, 801; **1920**, II, 405, 450.
Metallbörse **1920**, S. 1198, 1518/9, 1567.

Portugal

Zeitschr. f. angew. Chem. **1920**, II, 108.

Denmark

Chem.-Ztg. **1915**, S. 339, 495, 595; **1916**, S. 57, 912, 924; **1917**, S. 83, 195, 417, 455, 711, 828, 880; **1918**, S. 100, 191, 304, 335, 376, 472; **1919**, S. 172, 256, 716, 887; **1920**, S. 344, 364, 687, 715.
Zeitschr. f. angew. Chem. **1918**, III, 418, 434, 454, 619; **1919**, II, 7, 108; **1920**, II, 473.
Metallbörse **1920**, S. 1318.

Iceland

Chem.-Ztg. **1918**, S. 371; **1920**, S. 58.
Zeitschr. f. angew. Chem. **1918**, III, 210.
Die Technik in der Landwirtschaft **1919**, S. 228.

Netherlands

Chem.-Ztg. **1915**, S. 315; **1917**, S. 719; **1918**, S. 76, 167, 263, 297, 371, 419, 555, 572; **1919**, S. 43, 487, 503, 783; **1920**, S. 88, 279, 296.
Zeitschr. f. angew. Chem. **1918**, III, 216, 265, 282, 300, 338, 384/5, 392, 573, 618; **1919**, II, 21, 43, 440, 506, 567, 673, 736, 790; **1920**, II, 151, 226, 404.
Chem. Ind. **1916**, Bd. 39, S. 174.
Journ. f. Gasbel. **1919**, Bd. 62, S. 128.
Metallb. **1920**, S. 1854.

Chem.-Ztg. **1915**, S. 148, 367, 439, 701; **1916**, S. 120, 142, 455, 603, 662, 1099; Repert. S. 285; **1917**, S. 342; **1920**, S. 143.

Zeitschr. f. angew. Chem. **1918**, II, 274 ; III, 597 ; **1919**, II, 402, 577, 666 ; **1920**, II, 163.
Umschau **1919**, S. 718.
Metallbörse **1920**, S. 1359, 1615/6, 2104/5.
Die Technik in der Landwirtschaft **1920**, S. 619.

Finland

Chem.-Ztg. **1915**, S. 712, 800 ; **1918**, S. 588, 603 ; **1919**, S. 403 ; chem -techn. Übers. S. 197 ; **1920**, S. 208.
Zeitschr. f. angew. Chem. **1918**, III, 509, 573 ; **1919**, II, 725.

Esthonia

Chem. Ind. **1921**, S. 76.

Bulgaria

Zeitschr. f. angew. Chem. **1918**, III, 502.
See also Supplement, pp. 251 253.

Chapter XI.—The Development of the Nitrogen Industry in the United States of North America

Chem.-Ztg. **1915**, S. 523, 643, 864, 919 ; Repert. S. 103, 310 ; **1916**, S. 269, 592, 827, 847, 927, 970/1, Repert. S. 114, 137 ; **1917**, S. 157, 179, 243, 254/5, 292, 334, 444, 456, 480, 486, 549, 583/4, 686, 743, 828 ; **1918**, S. 61, 73, 91, 109, 125, 134, 179, 221, 227, 239, 377, 418, 432, 479, 495, 531, 568, 604 ; **1919**, S. 7, 12, 36, 208, 244, 298, 419, 502, 526/7, 536, 561, 640, 652, 660, 663, 670, 686, 701, 703, 806, 832, 867 ; **1920**, S. 8, 25, 30, 31, 36, 135, 172, 177, 183, 204, 292, 296, 314, 327, 364, 386, 423, 485/6, 491, 546, 583, 596, 618, 620, 631, 687, 720, 812, 887.
Zeitschr. f. angew. Chem. **1918**, III, 29, 62/3, 98, 210, 263, 384, 402, 417, 470, 482, 490, 514, 520, 526, 539, 543, 550, 590, 614 ; **1919**, II, 14, 115, 121, 147, 154/5, 287, 334/5, 503, 513, 555, 587, 590, 648, 672, 682, 736, 774, 794 ; **1920**, II, 5, 13, 59, 61, 71, 87, 95, 99, 115, 136, 138, 164, 215, 249, 299, 309, 330, 370, 399, 419, 439.
Chem. and Met. Eng. **1915**, January ; **1917**, Bd. 16, S. 232 ; **1919**, Bd. 20, S. 320, 819 ; **1920**, Bd. 22, S. 369.
J. Ind. Eng. Chem. **1914**, Bd. 6, S. 415.
Eng. and Min. Journ. **1915**, S. 476.
Electr. World **1919**, Bd. 73, S. 677, 729.
Journ. f. Gasbel. **1915**, S. 129, 133, 135 ; **1917**, Bd. 60, S. 479.
Ernährung der Pflanze **1916**, Bd. 12, S. 149.
Chem. Ind. **1918**, S. 1765ff. ; **1919**, S. 99, 293/4, 295.
Südd. Ind.-Blatt **1920**, S. 1387ff.
Ch. Ztrlbl. **1919**, II, 193, 243, 515, 659, 836 ; IV, 72, 430, 1069 ; **1920**, II, 799.
Umschau **1919**, S. 7, 268, 380, 422, 442, 443, 487.
Techn. Rundsch. (Berl. Tagebl.) **1919**, S. 72.
Die Technik in der Landwirtschaft **1920**, S. 714.
Metallbörse **1920**, S. 879, 961, 1161, 1280, 1399 ; **1921**, S. 310, 401.
See also Supplement, pp. 300–301.

Chapter XII.—The Canadian Nitrogen Industry

Chem. Ind. **1912**, S. 294.
Chem.-Ztg. **1915**, S. 39, 612 ; **1916**, S. 131 ; **1917**, S. 538, 719, 899 ; **1918**, S. 507 ; **1919**, S. 526, 791, 867, 887, 896, 927 ; **1920**, S. 71, 142, 240, 619.

Zeitschr. f. angew. Chem. **1918**, III, 82, 390, 533, 617 ; **1919**, II, 318, 661 ; **1920**, II, 34, 211, 260, 369, 374.
Umschau **1919**, S. 735.
Metallbörse **1920**, S. 840.
Ch. Ztrlbl. **1920**, IV, 79.
See also Supplement, p. 305.

Chapter XIII.—The Nitrogen Industry in South America (excepting Chile)

Chem.-Ztg. **1916**, S. 335 ; **1917**, S. 100 ; **1918**, S. 239, 251, 299 ; **1919**, S. 632, 652, 686 ; **1920**, S. 172, 685.
Zeitschr. f. angew. Chem. **1918**, III, 263, 366, 572 ; **1919**, II, 20, 81, 192, 623 ; **1920**, II, 310, 318, 379.
Chem. Ind. **1921**, S. 13.
Metallbörse **1920**, S. 1400.
See also Supplement, pp. 307–308.

Chapter XIV.—The Nitrogen Industry in Africa

Chem.-Ztg. **1916**, S. 548 ; **1918**, S. 35 ; **1919**, S. 431, 520, 716, 812, 928 ; **1920**, S. 172, 548, 687.
Zeitschr. f. angew. Chem. **1918**, III, 287, 307, 430 ; **1919**, II, 362, 431, 472, 537, 648, 705, 722, 822/3 ; **1920**, II, 87.
Chem. Ind. **1921**, S. 13.

Chapter XV.—The Nitrogen Industry in Asia

Chem.-Ztg. **1915**, S. 128 ; **1916**, S. 1008 ; **1917**, S. 83, 312, 474, 495, 588, 595, 616, 623, 828 ; **1918**, S. 35, 40, 329, 347, 400, 418, 437, 472, 479 ; **1919**, S. 228, 438, 462, 503, 607, 660, 671, 775, 806, 867, 896 ; **1920**, S. 24, 47, 48, 143, 152, 171, 172, 547, 596, 708, 804 ; **1921**, S. 116, 428.
Zeitschr. f. angew. Chem. **1918**, III, 5, 257, 299, 340, 458, 521, 534, 659 ; **1919**, II, 15, 82, 93, 142, 321, 496, 503, 570, 633, 681, 735 ; **1920**, II, 10, 38, 92, 114, 119, 164, 170, 229, 248, 284, 309, 318, 377, 442, 461, 473.
Chem. Ind. **1920**, S. 83/4 ; **1921**, S. 5.
Metallbörse **1920**, S. 1159, 1243, 1280, 1291 ; **1921**, S. 161.
Südd. Ind.-Blatt **1920**, S. 1817.
See also Supplement, p. 322.

Chapter XVI.—The Nitrogen Industry in Australasia

Chem.-Ztg. **1917**, S. 703 ; **1918**, S. 112, 167, 359, 407, 536 ; **1919**, S. 298, 407, 695.
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Chapter XVII.—The World's Nitrogen Industry

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See also Supplement, p. 330.

Chapter XVIII.—The Cyanamide Industry

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CHAPTER XIX.—THE NITRIDE PROCESSES

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See also Supplement, p. 433.

CHAPTER XX.—THE HABER-BOSCH AMMONIA SYNTHESIS

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CHAPTER XXI.—THE CYANIDE PROCESSES

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CHAPTER XXII.—THE MANUFACTURE OF NITROGEN AND HYDROGEN

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See also Supplement, pp. 554–556.

Chapter XXIII.—The Former Methods of Manufacture of Nitric Acid from Nitrate

The most important recent literature is given in the text.
See also Supplement, p. 559.

Chapter XXIV.—The Arc Processes

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Chapter XXV.—The Catalytic Oxidation of Ammonia to Nitric Acid

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Chapter XXVI.—The Conversion of Nitrogen Oxides into Nitric Acid

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See also Supplement, pp. 683 684.

Chapter XXVII.—The Salts of Ammonia and of the Nitrogen Oxy-Acids

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See also Supplement, pp. 692–694.

CHAPTER XXVIII.—CONCLUSION

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